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(54) **Title of the Invention:** Olefin polymerization catalyst and method for the
polymerization of olefins

(57) Abstract

(Problem) To provide an olefin polymerization catalyst and method that exhibit a high polymerization activity and that yield an olefin (co)polymer that has a broad molecular weight distribution and hence an excellent moldability.

(Solution) An olefin polymerization catalyst that comprises

(A) transition metal compound from Group 4 of the Periodic Table that contains a ligand that has the cyclopentadienyl skeleton;

(B) transition metal amide compound represented by

$(R_2N)_kMX_{j-k}$ [see Translator's Note below]

wherein

M is a transition metal from Groups 3-6 of the Periodic Table,

j is the valence of M,

k is an integer from 1 to j,

R is, for example, hydrocarbyl, and

X is, for example, halogen; and

(C) at least one compound selected from

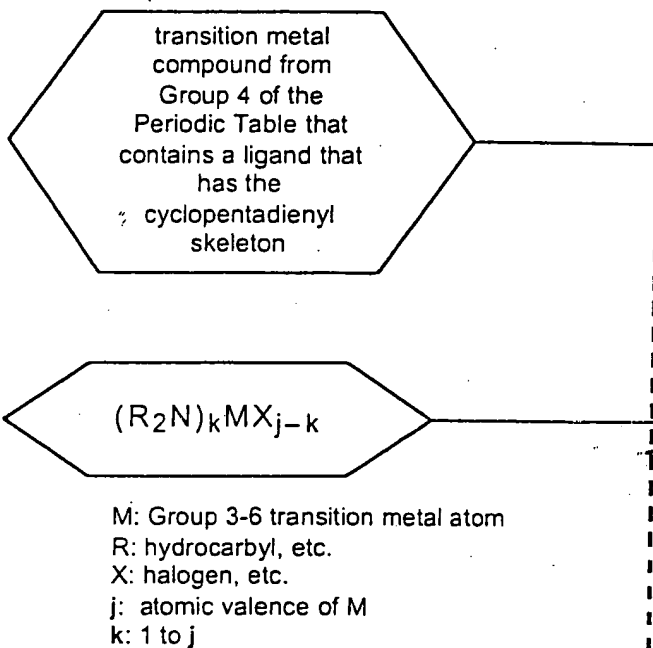
organometal compounds,

organoaluminumoxy compounds, and

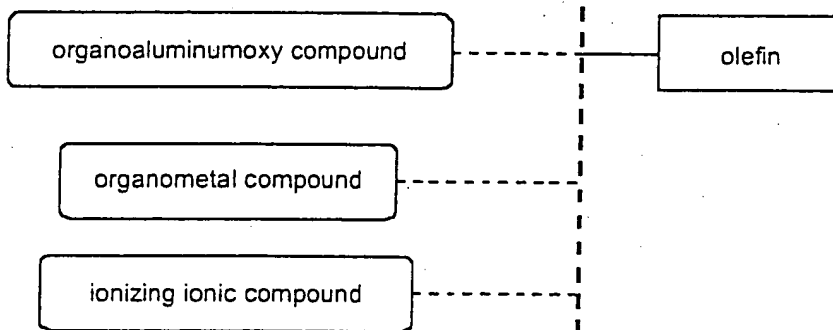
compounds that react with the aforesaid (A) or (B) to form an ion pair.

Translator's Note. The formula $(R_2N)_kMX_{j-k}$ does not directly match either (I) or (I-1) in component (B) in claim 1 (see page 4 of this translation), and it does not seem possible to reasonably subsume either (I) or (I-1) under $(R_2N)_kMX_{j-k}$. In addition, the graphic in this Abstract (see page 3 of this translation) does not entirely agree with the contents of the present invention. For example, the graphic identifies component (B) as an organometal component and component (C) as a microparticulate carrier, while the present invention actually identifies (B) as a transition metal amide compound and (C) as the organometal component. It would appear that this Abstract and associated graphic have been lifted from another filing by Mitsui Chemicals without having been entirely adapted to the contents of the present invention. Figure 1 is identical to the graphic in the Abstract and thus is heir to the same infelicities.

(A) Transition metal component



(B) Organometal component



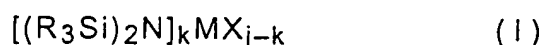
(C) Third component

(microparticulate carrier)

Claims

(Claim 1) Olefin polymerization catalyst that characteristically comprises.

- (A) a transition metal compound from Group 4 of the Periodic Table that contains a ligand that has the cyclopentadienyl skeleton;
- (B) a transition metal amide compound represented by general formula (I) or (I-1)



wherein

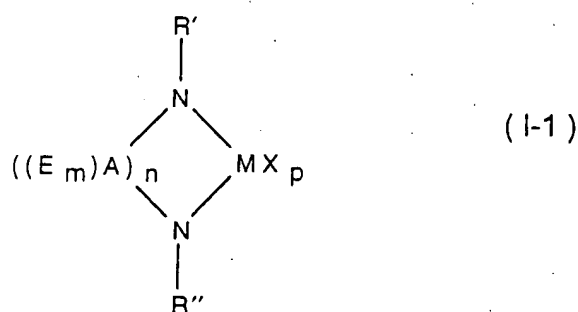
M is a transition metal atom from Groups 3-6 of the Periodic Table,

j is the valence of the transition metal atom M,

k is an integer from 1 to j,

each R is independently selected from hydrocarbyl and halogenated hydrocarbyl wherein two of the groups R may be connected to each other to form a ring, and

X represents the hydrogen atom, halogen atoms, C₁ to C₂₀ hydrocarbyl, C₁ to C₂₀ halogenated hydrocarbyl, an oxygen-containing group, a sulfur-containing group, or a silicon-containing group, wherein when j - k ≥ 2 the X's may be the same as each other or may differ from one another,



wherein

M represents a transition metal atom from Groups 3-6 of the Periodic Table,

R' and R'' are each independently selected from the hydrogen atom, hydrocarbyl, halogenated hydrocarbyl, organosilyl groups, and substituents that contain at least 1 element selected from nitrogen, oxygen, phosphorus, sulfur, and silicon,

m is an integer from 0 to 2,

n is an integer from 1 to 5,

A is an atom from Groups 13-16 of the Periodic Table, wherein when $n \geq 2$ the plurality of said A's may be the same as each other or may differ from one another, and

E is a substituent that contains at least 1 element selected from carbon, hydrogen, oxygen, halogen, nitrogen, sulfur, phosphorus, boron, and silicon, wherein when a plurality of groups represented by E are present said plurality of groups represented by E may be the same as each other or may differ from one another and two or more groups represented by E may be connected to each other to form a ring; and

(C) at least one compound selected from

(C-1) organometal compounds,

(C-2) organoaluminumoxy compounds, and

(C-3) compounds that react with the aforesaid transition metal compound (A) or transition metal amide compound (B) to form an ion pair.

(Claim 2) Method for the polymerization of olefins, characterized by effecting the polymerization or copolymerization of olefin in the presence of an olefin polymerization catalyst as described in claim 1.

Detailed Description of the Invention

(0001)

Field of the Invention

The present invention relates to an olefin polymerization catalyst and to a method for the polymerization of olefins using this catalyst. More particularly, this invention relates to a novel olefin polymerization catalyst that exhibits a high polymerization activity and that produces an olefin (co)polymer that has a broad molecular weight distribution. This invention also relates to a method for the polymerization of olefins that uses this novel catalyst.

(0002)

Technical Background of the Invention

Titanium catalysts comprising a titanium compound and an organoaluminum compound and vanadium catalysts comprising a vanadium compound and an organoaluminum compound are already known as catalysts for the production of olefin polymers such as ethylene polymers and ethylene- α -olefin copolymers.

(0003)

Ziegler catalysts comprising a metallocene compound (e.g., a zirconocene) and an organoaluminumoxy compound (aluminoxane) are known as catalysts capable of producing olefin polymers at high polymerization activities.

(0004)

With regard to the very newest olefin polymerization catalysts, for example, olefin polymerization catalysts comprising an aluminoxane and a titanium amide compound containing the titanium-nitrogen bond have been described in Japanese Laid Open (Unexamined or Kokai or A) Patent Application Number Hei 8-245713 (245,713/1996).

(0005)

In addition, a Group 4 organometal complex that contains the bis(borylamido) ligand $[\text{Mes}_2\text{BNCH}_2\text{CH}_2\text{NBMe}_2]^{-2}$ is described in Organometallics, 1996, 15, 562-569, which also reports that this complex exhibits a weak ethylene polymerization activity.

(0006)

Polyolefins such as ethylene polymers exhibit an excellent mechanical strength and chemical resistance and for this reason are used as a variety of molding materials. Catalysts comprising aluminoxane and a transition metal amide compound such as the aforementioned titanium amide compound exhibit high polymerization activities, but they give olefin polymers with a narrow molecular weight distribution that as a consequence do not always have a good moldability. As a result, there has been desire for the appearance of an improved transition metal amide compound-containing catalyst that would have the ability to produce olefin polymer with a broad molecular weight distribution and hence an excellent moldability, and that would achieve this outcome without sacrificing the high polymerization activity.

(0007)

Objects of the Invention

The present invention was developed in view of the prior art described above and has as an object the introduction of an olefin polymerization catalyst that exhibits a high polymerization activity and that provides olefin (co)polymer that has a broad molecular weight distribution and an excellent moldability.

(0008)

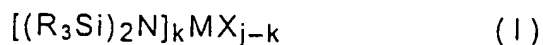
Another object of this invention is to provide a method for the polymerization of olefins that uses the aforesaid catalyst with its excellent properties.

(0009)

Disclosure of the Invention

The olefin polymerization catalyst according to the present invention characteristically comprises

- (A) a transition metal compound from Group 4 of the Periodic Table that contains a ligand that has the cyclopentadienyl skeleton;
- (B) a transition metal amide compound represented by general formula (I) or (I-1)



wherein

M is a transition metal atom from Groups 3-6 of the Periodic Table,

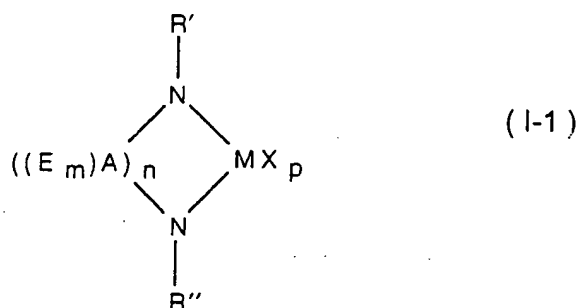
j is the valence of the transition metal atom M ,

k is an integer from 1 to j ,

each R is independently selected from hydrocarbyl and halogenated hydrocarbyl wherein two of the groups R may be connected to each other to form a ring, and

X represents the hydrogen atom, halogen atoms, C_1 to C_{20} hydrocarbyl, C_1 to C_{20} halogenated hydrocarbyl, an oxygen-containing group, a sulfur-containing group, or a silicon-containing group, wherein when $j - k \geq 2$ the X 's may be the same as each other or may differ from one another,

(0010)



(0011)

wherein

M represents a transition metal atom from Groups 3-6 of the Periodic Table,

R' and R'' are each independently selected from the hydrogen atom, hydrocarbyl, halogenated hydrocarbyl, organosilyl groups, and substituents that contain at least 1 element selected from nitrogen, oxygen, phosphorus, sulfur, and silicon,

m is an integer from 0 to 2,

n is an integer from 1 to 5,

A is an atom from Groups 13-16 of the Periodic Table, wherein when $n \geq 2$ the plurality of said A 's may be the same as each other or may differ from one another, and

E is a substituent that contains at least 1 element selected from carbon, hydrogen, oxygen, halogen, nitrogen, sulfur, phosphorus, boron, and silicon, wherein when a plurality of groups represented by E are present said plurality of groups represented by E may be the same as each other or may differ from one another and two or more groups represented by E may be connected to each other to form a ring; and

(C) at least one compound selected from

(C-1) organometal compounds,

(C-2) organoaluminumoxy compounds, and

(C-3) compounds that react with the aforesaid transition metal compound (A) or transition metal amide compound (B) to form an ion pair.

(0012)

The inventive olefin polymerization catalyst exhibits a high polymerization activity and affords olefin (co)polymer that exhibits a broad molecular weight distribution and that, when two or more olefins are polymerized, exhibits a narrow composition distribution.

(0013)

The method according to the present invention for the polymerization of olefins is characterized by effecting the polymerization or copolymerization of olefin in the presence of the above-described catalyst.

(0014)

Detailed Description of the Invention

The inventive olefin polymerization catalyst and the inventive olefin polymerization method using said catalyst are described hereinbelow in detail.

(0015)

As used herein, the term "polymerization" encompasses both homopolymerization and copolymerization and the term "polymer" encompasses both homopolymers and copolymers.

(0016)

The inventive olefin polymerization catalyst is formed from

- (A) a transition metal compound from Group 4 of the Periodic Table that contains a ligand that has the cyclopentadienyl skeleton;
- (B) a transition metal amide compound; and
- (C) at least one compound selected from
 - (C-1) organometal compounds,
 - (C-2) organoaluminumoxy compounds, and
 - (C-3) compounds that react with the aforesaid transition metal compound (A) or transition metal amide compound (B) to form an ion pair.

(0017)

Each of the catalyst components that form the inventive olefin polymerization catalyst will be described first.

(A) The transition metal compound from Group 4 of the Periodic Table that contains a ligand that has the cyclopentadienyl skeleton

The component (A) used in this invention, defined as a transition metal compound from Group 4 of the Periodic Table that contains a ligand that has the cyclopentadienyl skeleton, is a transition metal compound described by the following general formula (II-1).



M^1 in this formula represents a transition metal atom selected from Group 4 of the Periodic Table and specifically is zirconium, titanium, or hafnium wherein zirconium is preferred.

(0019)

The subscript x is the atomic valence of the transition metal atom M^1 and represents the number of ligands L coordinated to the transition metal atom M^1 . L denotes the ligands coordinated to the transition metal atom, and at least one of the ligands L is a ligand having the cyclopentadienyl skeleton (hereinafter referred to as cyclopentadienyl-based ligand). Ligands L other than the cyclopentadienyl-based ligand comprise C_1 to C_{20} hydrocarbyl, C_1 to C_{20} halogenated hydrocarbyl, oxygen-containing groups, sulfur-containing groups, silicon-containing groups, halogen atoms, and the hydrogen atom.

(0020)

The cyclopentadienyl-based ligand can be exemplified by the cyclopentadienyl group; alkyl-substituted cyclopentadienyl groups such as methylcyclopentadienyl, dimethylcyclopentadienyl, trimethylcyclopentadienyl, tetramethylcyclopentadienyl, pentamethylcyclopentadienyl, ethylcyclopentadienyl, methylethylcyclopentadienyl, propylcyclopentadienyl, methylpropylcyclopentadienyl, butylcyclopentadienyl, methylbutylcyclopentadienyl, and hexylcyclopentadienyl; and also by indenyl, 4,5,6,7-tetrahydroindenyl, and fluorenyl. These groups can be substituted by, for example, C_1 to C_{20} (halogenated) hydrocarbyl, oxygen-containing groups, sulfur-containing groups, silicon-containing groups, and halogen atoms.

(0021)

When the compound (II-1) contains two or more cyclopentadienyl-based ligands, two of these cyclopentadienyl-based ligands can be connected to each other through a divalent bridging group such as a (substituted) alkylene group or a (substituted) silylene group. Such transition metal compounds in which two cyclopentadienyl-based ligands are interconnected through a divalent bridging group can be exemplified by transition metal compounds with general formula (II-3), vide infra.

(0022)

The ligands L other than the cyclopentadienyl-based ligand can be specifically exemplified as follows. The C₁ to C₂₀ hydrocarbyl can be exemplified by alkyl, cycloalkyl, alkenyl, arylalkyl, and aryl. Each of these categories can be more specifically exemplified as follows: methyl, ethyl, propyl, butyl, hexyl, octyl, nonyl, dodecyl, and eicosyl for alkyl; cyclopentyl, cyclohexyl, norbornyl, and adamantyl for cycloalkyl; vinyl, propenyl, and cyclohexenyl for alkenyl; benzyl, phenylethyl, and phenylpropyl for arylalkyl; and phenyl, tolyl, dimethylphenyl, trimethylphenyl, ethylphenyl, propylphenyl, biphenyl, naphthyl, methylnaphthyl, anthryl, and phenanthryl for aryl.

(0023)

The C₁ to C₂₀ halogenated hydrocarbyl can be exemplified by groups as afforded by halogen substitution into the aforementioned C₁ to C₂₀ hydrocarbyl. The oxygen-containing groups can be exemplified by the hydroxyl group; alkoxy groups such as methoxy, ethoxy, propoxy, and butoxy; aryloxy groups such as phenoxy, methylphenoxy, dimethylphenoxy, and naphthoxy; and arylalkoxy groups such as phenylmethoxy and phenylethoxy.

(0024)

The sulfur-containing groups can be exemplified by substituents as afforded by substituting sulfur for the oxygen in the foregoing oxygen-containing groups, and also by sulfonate groups such as methylsulfonate, trifluoromethanesulfonate, phenylsulfonate, benzylsulfonate, p-toluenesulfonate, trimethylbenzenesulfonate, triisobutylbenzenesulfonate, p-chlorobenzenesulfonate, and pentafluorobenzenesulfonate; and by sulfinatate groups such as methylsulfinatate, phenylsulfinatate, benzylsulfinatate, p-toluenesulfinatate, trimethylbenzenesulfinatate, and pentafluorobenzenesulfinatate.

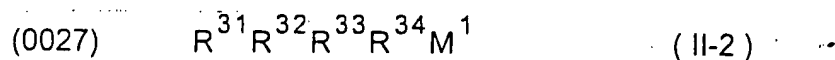
(0025)

The silicon-containing groups can be exemplified by monohydrocarbyl-substituted silyl such as

methylsilyl and phenylsilyl; dihydrocarbyl-substituted silyl such as dimethylsilyl and diphenylsilyl; trihydrocarbyl-substituted silyl such as trimethylsilyl, triethylsilyl, tripropylsilyl, tricyclohexylsilyl, triphenylsilyl, dimethylphenylsilyl, methyldiphenylsilyl, tritolylsilyl, and trinaphthylsilyl; the silyl ethers of hydrocarbyl-substituted silyl, such as trimethylsilyl ether; Si-substituted alkyl groups such as trimethylsilylmethyl; and Si-substituted aryl groups such as trimethylsilylphenyl.

(0026)

The halogen atoms can be exemplified by fluorine, chlorine, bromine, and iodine. When, for example, the atomic valence of the transition metal is 4, the transition metal compound under consideration is more specifically represented by the following general formula (II-2).



As above, M^1 in this formula represents a transition metal atom selected from Group 4 of the Periodic Table and is preferably the zirconium atom.

(0028)

R^{31} represents a cyclopentadienyl-based group (ligand), while R^{32} , R^{33} , and R^{34} are each independently selected from cyclopentadienyl-based groups (ligands), C_1 to C_{20} (halogenated) hydrocarbyl, the oxygen-containing groups, the sulfur-containing groups, the silicon-containing groups, halogen atoms, and the hydrogen atom.

(0029)

Among transition metal compounds (II-2), compounds in which at least one of R^{32} , R^{33} , and R^{34} is a cyclopentadienyl-based group (ligand), for example, compounds in which R^{31} and R^{32} are cyclopentadienyl-based groups (ligands), are preferably used by the present invention. In addition, when R^{31} and R^{32} are both cyclopentadienyl-based groups (ligands), R^{33} and R^{34} are preferably cyclopentadienyl-based groups, alkyl, cycloalkyl, alkenyl, arylalkyl, aryl, alkoxy, aryloxy, trialkylsilyl, sulfonate groups, halogen, or the hydrogen atom.

(0030)

Transition metal compounds (II-1) in which M^1 = zirconium can be exemplified by the following specific compounds:

bis(indenyl)zirconium dichloride,

bis(indenyl)zirconium dibromide,

bis(indenyl)zirconium bis(p-toluenesulfonate),
bis(4,5,6,7-tetrahydroindenyl)zirconium dichloride,
bis(fluorenyl)zirconium dichloride,
bis(cyclopentadienyl)zirconium dichloride,
bis(cyclopentadienyl)zirconium dibromide,
bis(cyclopentadienyl)methylzirconium monochloride,
bis(cyclopentadienyl)ethylzirconium monochloride,
bis(cyclopentadienyl)cyclohexylzirconium monochloride,
bis(cyclopentadienyl)phenylzirconium monochloride,
bis(cyclopentadienyl)benzylzirconium monochloride,
bis(cyclopentadienyl)zirconium monochloride monohydride,
bis(cyclopentadienyl)methylzirconium monohydride,
bis(cyclopentadienyl)dimethylzirconium,
bis(cyclopentadienyl)diphenylzirconium,
bis(cyclopentadienyl)dibenzylzirconium,
bis(cyclopentadienyl)zirconium methoxychloride,
bis(cyclopentadienyl)zirconium ethoxychloride,
bis(cyclopentadienyl)zirconium bis(methanesulfonate),
bis(cyclopentadienyl)zirconium bis(p-toluenesulfonate),
bis(cyclopentadienyl)zirconium bis(trifluoromethanesulfonate),
bis(methylcyclopentadienyl)zirconium dichloride,
bis(dimethylcyclopentadienyl)zirconium dichloride,
bis(dimethylcyclopentadienyl)zirconium ethoxychloride,
bis(dimethylcyclopentadienyl)zirconium bis(trifluoromethanesulfonate),
bis(ethylcyclopentadienyl)zirconium dichloride,
bis(methylethylcyclopentadienyl)zirconium dichloride,
bis(propylcyclopentadienyl)zirconium dichloride,
bis(methylpropylcyclopentadienyl)zirconium dichloride,
bis(butylcyclopentadienyl)zirconium dichloride,
bis(methylbutylcyclopentadienyl)zirconium dichloride,
bis(methylbutylcyclopentadienyl)zirconium bis(methanesulfonate),
bis(trimethylcyclopentadienyl)zirconium dichloride,
bis(tetramethylcyclopentadienyl)zirconium dichloride,
bis(pentamethylcyclopentadienyl)zirconium dichloride,
bis(hexylcyclopentadienyl)zirconium dichloride, and
bis(trimethylsilylcyclopentadienyl)zirconium dichloride.

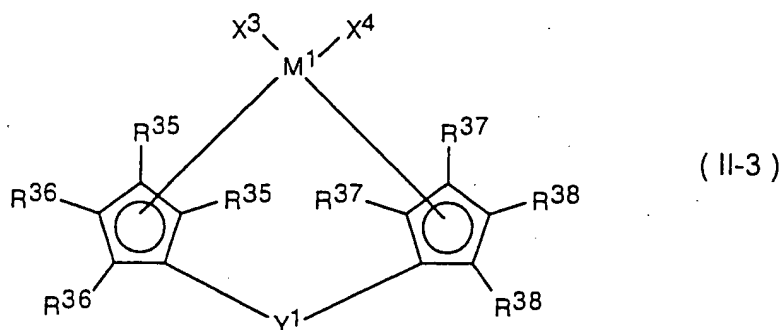
(0031)

In the preceding examples, the substitution pattern for the disubstituted cyclopentadienyl ring includes the 1,2- and 1,3-substitution patterns, while the trisubstitution pattern includes the 1,2,3- and 1,2,4-substitution patterns. In addition, alkyl groups such as propyl and butyl include the n-, i-, sec-, and tert-isomers.

(0032)

Other examples include the compounds afforded by replacing the zirconium in the preceding zirconium compounds with titanium or hafnium. Compounds with formula (II-3) can be provided as examples of the transition metal compounds in which two cyclopentadienyl-based ligands are connected to each other through a divalent bridging group.

(0033)



(0034)

M^1 in this formula represents a transition metal atom from Group 4 of the Periodic Table and specifically is zirconium, titanium, or hafnium and is preferably zirconium. The groups R^{35} , R^{36} , R^{37} , and R^{38} are each independently selected from C_1 to C_{20} hydrocarbyl, C_1 to C_{20} halogenated hydrocarbyl, oxygen-containing groups, sulfur-containing groups, silicon-containing groups, nitrogen-containing groups, phosphorus-containing groups, halogen atoms, and the hydrogen atom. Among these groups R^{35} , R^{36} , R^{37} , and R^{38} , some of the groups adjacent to each other may be interconnected to form a ring together with the carbon atoms to which said groups are bonded. Each of the groups R^{35} , R^{36} , R^{37} , and R^{38} is specified at two locations, and in each case the two groups, for example, R^{35} and R^{35} , may be the same as each other or may differ from one another. Among the groups designated by R, those with the same superscript represent a preferred combination for ring formation through their interconnection.

(0035)

The C₁ to C₂₀ hydrocarbyl can be exemplified by the same alkyl, cycloalkyl, alkenyl, arylalkyl, and aryl as provided above in the discussion of L.

(0036)

The rings formed by the interconnection of these hydrocarbyl groups can be exemplified by condensed ring groups such as the benzene ring, naphthalene ring, acenaphthene ring, and indene ring and by groups as afforded by replacing hydrogen in these condensed ring groups with an alkyl group such as methyl, ethyl, propyl, and butyl.

(0037)

The C₁ to C₂₀ halogenated hydrocarbyl can be exemplified by groups as afforded by substituting halogen into the aforementioned C₁ to C₂₀ hydrocarbyl. The oxygen-containing groups can be exemplified by the hydroxyl group and the same alkoxy, aryloxy, and arylalkoxy groups as provided above in the discussion of L.

(0038)

The sulfur-containing groups can be exemplified by groups as afforded by replacing the oxygen in the aforementioned oxygen-containing groups with sulfur. The silicon-containing groups can be exemplified by the same monohydrocarbyl-substituted silyl, dihydrocarbyl-substituted silyl, trihydrocarbyl-substituted silyl, silyl ethers of hydrocarbyl-substituted silyl, Si-substituted alkyl groups, and Si-substituted aryl groups as provided above in the discussion of L.

(0039)

The nitrogen-containing groups can be exemplified by the amino group; alkylamino groups such as methylamino, dimethylamino, diethylamino, dipropylamino, dibutylamino, and dicyclohexylamino; and by arylamino and alkylarylamino groups such as phenylamino, diphenylamino, ditolylamino, dinaphthylamino, and methylphenylamino.

(0040)

The phosphorus-containing groups can be exemplified by phosphino groups such as dimethylphosphino and diphenylphosphino. The halogen atoms can be exemplified as in the discussion of L, *supra*.

(0041)

Among these possibilities, the hydrogen atom and C₁ to C₂₀ hydrocarbyl are preferred. The following are particularly preferred: C₁ to C₄ hydrocarbyl such as methyl, ethyl, propyl, and butyl; a benzene ring as formed by the interconnection of hydrocarbyl groups; and groups as afforded by substituting alkyl (e.g., methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, tert-butyl) for the hydrogen on the benzene ring generated by the interconnection of hydrocarbyl groups.

(0042)

X³ and X⁴ are each independently selected from C₁ to C₂₀ hydrocarbyl, C₁ to C₂₀ halogenated hydrocarbyl, oxygen-containing groups, sulfur-containing groups, silicon-containing groups, the hydrogen atom, and halogen atoms.

(0043)

The C₁ to C₂₀ hydrocarbyl can be exemplified by the same alkyl, cycloalkyl, alkenyl, arylalkyl, and aryl as provided above in the discussion of L.

(0044)

The C₁ to C₂₀ halogenated hydrocarbyl can be exemplified by groups as afforded by substituting halogen into the aforementioned C₁ to C₂₀ hydrocarbyl. The oxygen-containing groups can be exemplified by the hydroxyl group and the same alkoxy, aryloxy, and arylalkoxy groups as provided above in the discussion of L.

(0045)

The sulfur-containing groups can be exemplified by groups as afforded by replacing the oxygen in the aforementioned oxygen-containing groups with sulfur and by the same sulfonate and sulfinatate groups as provided above in the discussion of L. The silicon-containing groups can be exemplified by the same silicon-substituted alkyl groups and silicon-substituted aryl groups as provided above in the discussion of L.

(0046)

The halogen atoms can be exemplified by the same groups and atoms as in the discussion of L, *supra*. Among the various possibilities, halogen atoms, C₁ to C₂₀ hydrocarbyl, and sulfonate groups are preferred.

(0047)

Y^1 represents C_1 to C_{20} divalent hydrocarbyl, C_1 to C_{20} divalent halogenated hydrocarbyl, divalent silicon-containing groups, divalent germanium-containing groups, divalent tin-containing groups, $-O-$, $-CO-$, $-S-$, $-SO-$, $-SO_2-$, $-Ge-$, $-Sn-$, $-NR^{39}-$, $-P(R^{39})-$, $-P(O)(R^{39})-$, $-BR^{39}-$, or $-AlR^{39}-$ (each R^{39} is independently selected from C_1 to C_{20} hydrocarbyl, C_1 to C_{20} halogenated hydrocarbyl, the hydrogen atom, and halogen atoms).

(0048)

The C_1 to C_{20} divalent hydrocarbyl is specifically exemplified by alkylene groups such as methylene, dimethylmethylene, 1,2-ethylene, dimethyl-1,2-ethylene, 1,3-trimethylene, 1,4-tetramethylene, 1,2-cyclohexylene, and 1,4-cyclohexylene, and by arylalkylene groups such as diphenylmethylene and diphenyl-1,2-ethylene.

(0049)

The C_1 to C_{20} divalent halogenated hydrocarbyl can be specifically exemplified by groups as afforded by halogenation of the above-described C_1 to C_{20} divalent hydrocarbyl, for example, chloromethylene.

(0050)

The divalent silicon-containing groups can be exemplified by silylene; alkylsilylene, alkylarylsilylene, and arylsilylene groups such as methylsilylene, dimethylsilylene, diethylsilylene, di(n-propyl)silylene, di(i-propyl)silylene, di(cyclohexyl)silylene, methylphenylsilylene, diphenylsilylene, di(p-tolyl)silylene, and di(p-chlorophenyl)silylene; and alkylidisilylene, alkylaryldisilylene, and aryldisilylene groups such as tetramethyl-1,2-disilylene and tetraphenyl-1,2-disilylene.

(0051)

The divalent germanium-containing groups can be exemplified by groups as afforded by replacing the silicon in the above-described divalent silicon-containing groups with germanium. The divalent tin-containing groups can be exemplified by groups as afforded by replacing the silicon in the above-described divalent silicon-containing groups with tin.

(0052)

R^{39} represents the same C_1 to C_{20} hydrocarbyl, C_1 to C_{20} halogenated hydrocarbyl, and halogen atoms as discussed above for L. Particularly preferred among these are substituted silylene groups [sic] such as dimethylsilylene, diphenylsilylene, and methylphenylsilylene.¹

(0053)

Transition metal compounds (II-3) can be exemplified by the following specific compounds:

ethylenebis(indenyl)dimethylzirconium,
ethylenebis(indenyl)zirconium dichloride,
ethylenebis(indenyl)zirconium bis(trifluoromethanesulfonate),
ethylenebis(indenyl)zirconium bis(methanesulfonate),
ethylenebis(indenyl)zirconium bis(p-toluenesulfonate),
ethylenebis(indenyl)zirconium bis(p-chlorobenzenesulfonate),
ethylenebis(4,5,6,7-tetrahydroindenyl)zirconium dichloride,
isopropylidenebis(cyclopentadienyl)(fluorenyl)zirconium dichloride,
isopropylidenebis(cyclopentadienyl)(methylcyclopentadienyl)zirconium dichloride,
dimethylsilylenebis(cyclopentadienyl)zirconium dichloride,
dimethylsilylenebis(methylcyclopentadienyl)zirconium dichloride,
dimethylsilylenebis(dimethylcyclopentadienyl)zirconium dichloride,
dimethylsilylenebis(trimethylcyclopentadienyl)zirconium dichloride,
dimethylsilylenebis(indenyl)zirconium dichloride,
dimethylsilylenebis(indenyl)zirconium bis(trifluoromethanesulfonate),
dimethylsilylenebis(4,5,6,7-tetrahydroindenyl)zirconium dichloride,
dimethylsilylenebis(cyclopentadienyl)(fluorenyl)zirconium dichloride,
diphenylsilylenebis(indenyl)zirconium dichloride,
methylphenylsilylenebis(indenyl)zirconium dichloride,
rac-dimethylsilylenebis(2,3,5-trimethylcyclopentadienyl)zirconium dichloride,
rac-dimethylsilylenebis(2,4,7-trimethylcyclopentadienyl)zirconium dichloride,
rac-dimethylsilylenebis(2-methyl-4-tert-butylcyclopentadienyl)zirconium dichloride,
isopropylidene(cyclopentadienyl)(fluorenyl)zirconium dichloride,
dimethylsilylene(3-tert-butylcyclopentadienyl)(indenyl)zirconium dichloride,
isopropylidene(4-methylcyclopentadienyl)(3-methylindenyl)zirconium dichloride,

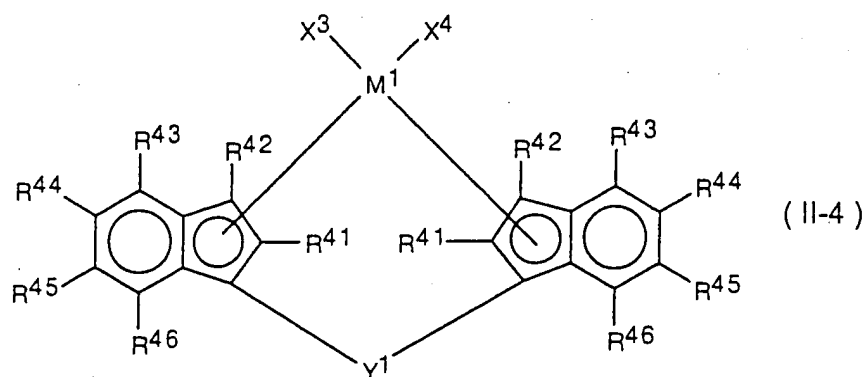
¹ Translator's Note. I can confirm that the Japanese source document does contain this list of substituted silylene groups as examples of R^{39} , although substituted silylene does not seem to fit with the classes of groups specified for R^{39} in section (0052).

isopropylidene(4-tert-butylcyclopentadienyl)(3-methylindenyl)zirconium dichloride,
 isopropylidene(4-tert-butylcyclopentadienyl)(3-tert-butylindenyl)zirconium dichloride,
 dimethylsilylene(4-methylcyclopentadienyl)(3-methylindenyl)zirconium dichloride,
 dimethylsilylene(4-tert-butylcyclopentadienyl)(3-methylindenyl)zirconium dichloride,
 dimethylsilylene(4-tert-butylcyclopentadienyl)(3-tert-butylindenyl)zirconium dichloride,
 dimethylsilylene(3-tert-butylcyclopentadienyl)(fluorenyl)zirconium dichloride, and
 isopropylidene(3-tert-butylcyclopentadienyl)(fluorenyl)zirconium dichloride.

(0054)

Other examples include the compounds afforded by replacing the zirconium in the preceding compounds with titanium or hafnium. The transition metal compounds (II-3) encompassed by the present invention can be more specifically exemplified by transition metal compounds with the following general formulas (II-4) and (II-5).

(0055)



(0056)

M^1 in this formula represents a transition metal atom from Group 4 of the Periodic Table and specifically is titanium, zirconium, or hafnium and is preferably zirconium. Each R^{41} is independently selected from C_1 to C_6 hydrocarbyl and can be specifically exemplified by alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, neopentyl, n-hexyl, and cyclohexyl, and by alkenyl such as vinyl and propenyl.

(0057)

Preferred among the preceding are alkyl in which the carbon atom bonded to the indenyl group is a primary carbon, more preferably C_1 to C_4 alkyl and particularly preferably methyl and ethyl.

(0058)

The groups R^{42} , R^{44} , R^{45} , and R^{46} are each independently selected from the hydrogen atom, halogen atoms, and the same C_1 to C_6 hydrocarbonyl as described above for R^{41} . Each R^{43} is independently selected from the hydrogen atom and C_6 to C_{16} aryl and can be specifically exemplified by phenyl, α -naphthyl, β -naphthyl, anthryl, phenanthryl, pyrenyl, acenaphthyl, phenalenyl, aceanthrylenyl, tetrahydronaphthyl, indanyl, and biphenylyl. Preferred among the preceding are phenyl, naphthyl, anthryl, and phenanthryl.

(0059)

These aryl groups can be substituted by halogen atoms such as fluorine, chlorine, bromine, and iodine; C_1 to C_{20} hydrocarbonyl, for example, alkyl (e.g., methyl, ethyl, propyl, butyl, hexyl, cyclohexyl, octyl, nonyl, dodecyl, eicosyl, norbornyl, and adamantyl), alkenyl (e.g., vinyl, propenyl, and cyclohexenyl), arylalkyl (e.g., benzyl, phenylethyl, and phenylpropyl), and aryl (e.g., phenyl, tolyl, dimethylphenyl, trimethylphenyl, ethylphenyl, propylphenyl, biphenyl, α - and β -naphthyl, methylnaphthyl, anthryl, phenanthryl, benzylphenyl, pyrenyl, acenaphthyl, phenalenyl, aceanthrylenyl, tetrahydronaphthyl, indanyl, and biphenylyl); and organosilyl such as trimethylsilyl, triethylsilyl, and triphenylsilyl.

(0060)

X^3 and X^4 are defined as for X^3 and X^4 in general formula (II-3) and may be the same as each other or may differ from one another. Among the various possibilities, halogen atoms and C_1 to C_{20} hydrocarbonyl are preferred.

(0061)

Y^1 is defined as for Y^1 in general formula (II-3). Among the various possibilities, divalent silicon-containing groups and divalent germanium-containing groups are preferred. Divalent silicon-containing groups are more preferred and alkylsilylene, alkylarylsilylene, and arylsilylene are even more preferred.

(0062)

The following are specific examples of transition metal compounds with general formula (II-4):

rac-dimethylsilylenebis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(α -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(β -naphthyl)indenyl)}zirconium dichloride,

rac-dimethylsilylenebis{1-(2-methyl-4-(1-anthryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(2-anthryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(9-anthryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(9-phenanthryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(p-fluorophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(pentafluorophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(p-chlorophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(m-chlorophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(o-chlorophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(o,p-dichlorophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(p-bromophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(p-tolyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(m-tolyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(o-tolyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(o,o'-dimethylphenyl)-1-indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(p-ethylphenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(p-isopropylphenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(p-benzylphenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(p-biphenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(m-biphenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(p-trimethylsilylenepheryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-(m-trimethylsilylenepheryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-phenyl-4-phenylindenyl)}zirconium dichloride,
rac-diethylsilylenebis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,
rac-di(i-propyl)silylenebis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,
rac-di(n-butyl)silylenebis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,
rac-dicyclohexylsilylenebis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,
rac-methylphenylsilylenebis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,
rac-diphenylsilylenebis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,
rac-di(p-tolyl)silylenebis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,
rac-di(p-chlorophenyl)silylenebis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,
rac-methylenebis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,
rac-ethylenebis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,
rac-dimethylgermylenebis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,
rac-dimethylstannylenebis{1-(2-methyl-4-phenylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-phenylindenyl)}zirconium dibromide,

rac-dimethylsilylenebis{1-(2-methyl-4-phenylindenyl)}dimethylzirconium,
rac-dimethylsilylenebis{1-(2-methyl-4-phenylindenyl)}methylzirconium chloride,
rac-dimethylsilylenebis{1-(2-methyl-4-phenylindenyl)}zirconium chloride SO₂Me,
rac-dimethylsilylenebis{1-(2-methyl-4-phenylindenyl)}zirconium chloride OSO₂Me,
rac-dimethylsilylenebis{1-(2-ethyl-4-phenylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(α -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(β -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(2-methyl-1-naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(5-acenaphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(9-anthryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(9-phenanthryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(o-methylphenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(m-methylphenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(p-methylphenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(2,3-dimethylphenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(2,4-dimethylphenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(2,5-dimethylphenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(2,4,6-trimethylphenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(o-chlorophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(m-chlorophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(p-chlorophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(2,3-dichlorophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(2,6-dichlorophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(3,5-dichlorophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(2-bromophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(3-bromophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(4-bromophenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(4-biphenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-(4-trimethylsilylphenyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-propyl-4-phenylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-propyl-4-(α -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-propyl-4-(β -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-propyl-4-(2-methyl-1-naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-propyl-4-(5-acenaphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-propyl-4-(9-anthryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-propyl-4-(9-phenanthryl)indenyl)}zirconium dichloride,

rac-dimethylsilylenebis{1-(2-i-propyl-4-phenylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-i-propyl-4-(α -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-i-propyl-4-(β -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-i-propyl-4-(8-methyl-9-naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-i-propyl-4-(5-acenaphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-i-propyl-4-(9-anthryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-i-propyl-4-(9-phenanthryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-s-butyl-4-phenylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-s-butyl-4-(α -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-s-butyl-4-(β -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-s-butyl-4-(2-methyl-1-naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-s-butyl-4-(5-acenaphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-s-butyl-4-(9-anthryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-s-butyl-4-(9-phenanthryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-pentyl-4-phenylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-pentyl-4-(α -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-butyl-4-phenylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-butyl-4-(α -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-butyl-4-(β -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-butyl-4-(2-methyl-1-naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-butyl-4-(5-acenaphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-butyl-4-(9-anthryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-butyl-4-(9-phenanthryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-i-butyl-4-phenylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-i-butyl-4-(α -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-i-butyl-4-(β -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-i-butyl-4-(2-methyl-1-naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-i-butyl-4-(5-acenaphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-i-butyl-4-(9-anthryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-i-butyl-4-(9-phenanthryl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-neopentyl-4-phenylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-neopentyl-4-(α -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-hexyl-4-phenylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-n-hexyl-4-(α -naphthyl)indenyl)}zirconium dichloride,
rac-methylphenylsilylenebis{1-(2-ethyl-4-phenylindenyl)}zirconium dichloride,
rac-methylphenylsilylenebis{1-(2-ethyl-4-(α -naphthyl)indenyl)}zirconium dichloride,

rac-methylphenylsilylenebis{1-(2-ethyl-4-(9-anthryl)indenyl)}zirconium dichloride,
rac-methylphenylsilylenebis{1-(2-ethyl-4-(9-phenanthryl)indenyl)}zirconium dichloride,
rac-diphenylsilylenebis{1-(2-ethyl-4-phenylindenyl)}zirconium dichloride,
rac-diphenylsilylenebis{1-(2-ethyl-4-(α -naphthyl)indenyl)}zirconium dichloride,
rac-diphenylsilylenebis{1-(2-ethyl-4-(9-anthryl)indenyl)}zirconium dichloride,
rac-diphenylsilylenebis{1-(2-ethyl-4-(9-phenanthryl)indenyl)}zirconium dichloride,
rac-diphenylsilylenebis{1-(2-ethyl-4-(4-biphenyl)indenyl)}zirconium dichloride,
rac-methylenebis{1-(2-ethyl-4-phenylindenyl)}zirconium dichloride,
rac-methylenebis{1-(2-ethyl-4-(α -naphthyl)indenyl)}zirconium dichloride,
rac-ethylenebis{1-(2-ethyl-4-phenylindenyl)}zirconium dichloride,
rac-ethylenebis{1-(2-ethyl-4-(α -naphthyl)indenyl)}zirconium dichloride,
rac-ethylenebis{1-(2-n-propyl-4-(α -naphthyl)indenyl)}zirconium dichloride,
rac-dimethylgermylbis{1-(2-ethyl-4-phenylindenyl)}zirconium dichloride,
rac-dimethylgermylbis{1-(2-ethyl-4-(α -naphthyl)indenyl)}zirconium dichloride, and
rac-dimethylgermylbis{1-(2-n-propyl-4-phenylindenyl)}zirconium dichloride.

(0063)

Other examples are the compounds generated by replacing the zirconium in the preceding compounds with titanium or hafnium. While the racemic form of the transition metal compound (II-4) will generally be used as the catalyst component by this invention, the R-form or S-form can also be used.

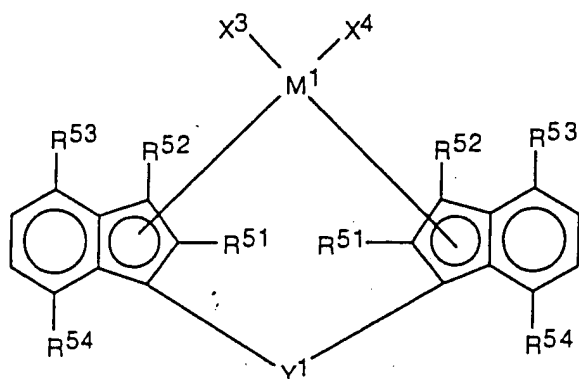
(0064)

The transition metal compound (II-4) can be synthesized according to Journal of Organometallic Chem., 288 (1985) pp. 63-67 and the examples and description of EP 320,762 A.

(0065)

The transition metal compound with general formula (II-5) will now be considered.

(0066)



(II-5)

(0067)

M¹ in the preceding formula is a transition metal atom from Group 4 of the Periodic Table and specifically is titanium, zirconium, or hafnium with zirconium being preferred. R⁵¹ and R⁵² are each independently selected from C₁ to C₂₀ hydrocarbyl, C₁ to C₂₀ halogenated hydrocarbyl, oxygen-containing groups, sulfur-containing groups, silicon-containing groups, nitrogen-containing groups, phosphorus-containing groups, halogen atoms, and the hydrogen atom. R⁵¹ and R⁵² can be specifically exemplified by the same atoms and groups as provided above for R³⁵ to R³⁸.

(0068)

Among the preceding possibilities, R⁵¹ is preferably C₁ to C₂₀ hydrocarbyl and particularly preferably is C₁ to C₃ hydrocarbyl, i.e., methyl, ethyl, or propyl.

(0069)

R⁵² is preferably the hydrogen atom or C₁ to C₂₀ hydrocarbyl and particularly preferably is the hydrogen atom or C₁ to C₃ hydrocarbyl, i.e., methyl, ethyl, or propyl.

(0070)

R⁵³ and R⁵⁴ are each independently selected from C₁ to C₂₀ alkyl and are specifically exemplified by cycloalkyl such as norbornyl and adamantyl and by alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, neopentyl, n-hexyl, cyclohexyl, octyl, nonyl, dodecyl, and eicosyl.

(0071)

Among the preceding possibilities, R⁵³ is preferably secondary or tertiary alkyl. X³ and X⁴

may be the same as each other or may differ from one another and are defined as for X^3 and X^4 in general formula (II-3).

(0072)

Y^1 is defined as for Y^1 in general formula (II-3). Specific examples of the transition metal compound (II-5) are as follows:

rac-dimethylsilylenebis{1-(2,7-dimethyl-4-ethylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,7-dimethyl-4-n-propylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,7-dimethyl-4-n-butylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,7-dimethyl-4-sec-butylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,7-dimethyl-4-t-butylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,7-dimethyl-4-n-pentylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,7-dimethyl-4-n-hexylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,7-dimethyl-4-cyclohexylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,7-dimethyl-4-methylcyclohexylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,7-dimethyl-4-phenylethylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,7-dimethyl-4-phenyldichloromethylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,7-dimethyl-4-chloromethylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,7-dimethyl-4-trimethylsilylmethylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,7-dimethyl-4-trimethylsiloxymethylindenyl)}zirconium dichloride,
rac-diethylsilylenebis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-di(i-propyl)silylenebis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-di(n-butyl)silylenebis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-di(cyclohexyl)silylenebis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-methylphenylsilylenebis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-methylphenylsilylenebis{1-(2,7-dimethyl-4-t-butylindenyl)}zirconium dichloride,
rac-diphenylsilylenebis{1-(2,7-dimethyl-4-t-butylindenyl)}zirconium dichloride,
rac-diphenylsilylenebis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-diphenylsilylenebis{1-(2,7-dimethyl-4-ethylindenyl)}zirconium dichloride,
rac-di(p-tolyl)silylenebis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-di(p-chlorophenyl)silylenebis{1-(2,7-dimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-i-propyl-7-ethylindenyl)}zirconium dibromide,
rac-dimethylsilylenebis{1-(2,3,7-trimethyl-4-ethylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,3,7-trimethyl-4-n-propylindenyl)}zirconium dichloride,

rac-dimethylsilylenebis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,3,7-trimethyl-4-n-butylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,3,7-trimethyl-4-sec-butylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,3,7-trimethyl-4-t-butylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,3,7-trimethyl-4-n-pentylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,3,7-trimethyl-4-n-hexylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,3,7-trimethyl-4-cyclohexylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,3,7-trimethyl-4-methylcyclohexylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,3,7-trimethyl-4-trimethylsilylmethylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,3,7-trimethyl-4-trimethylsiloxymethylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,3,7-trimethyl-4-phenylethylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,3,7-trimethyl-4-phenyldichloromethylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2,3,7-trimethyl-4-chloromethylindenyl)}zirconium dichloride,
rac-diethylsilylenebis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-di(i-propyl)silylenebis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-di(n-butyl)silylenebis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-di(cyclohexyl)silylenebis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-methylphenylsilylenebis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-methylphenylsilylenebis{1-(2,3,7-trimethyl-4-t-butylindenyl)}zirconium dichloride,
rac-diphenylsilylenebis{1-(2,3,7-trimethyl-4-t-butylindenyl)}zirconium dichloride,
rac-diphenylsilylenebis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-diphenylsilylenebis{1-(2,3,7-trimethyl-4-ethylindenyl)}zirconium dichloride,
rac-di(p-tolyl)silylenebis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-di(p-chlorophenyl)silylenebis{1-(2,3,7-trimethyl-4-i-propylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4-i-propyl-7-methylindenyl)}dimethylzirconium,
rac-dimethylsilylenebis{1-(2-methyl-4-i-propyl-7-methylindenyl)}methylzirconium chloride,
rac-dimethylsilylenebis{1-(2-methyl-4-i-propyl-7-methylindenyl)}zirconium
bis(methanesulfonate),
rac-dimethylsilylenebis{1-(2-methyl-4-i-propyl-7-methylindenyl)}zirconium bis(p-
phenylsulfinate),
rac-dimethylsilylenebis{1-(2-methyl-3-methyl-4-i-propyl-7-methylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methyl-4,6-di-i-propylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-ethyl-4-i-propyl-7-methylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-phenyl-4-i-propyl-7-methylindenyl)}zirconium dichloride,
rac-dimethylsilylenebis{1-(2-methylindenyl)}zirconium dichloride,
rac-ethylenebis{1-(2,4,7-trimethylindenyl)}zirconium dichloride, and

rac-isopropylidenebis(1-(2,4,7-trimethylindenyl))zirconium dichloride.

(0073)

Other examples include compounds generated by replacing the zirconium in the preceding compounds with titanium or hafnium. Among the various possibilities, compounds having a branched alkyl, e.g., i-propyl, sec-butyl, or tert-butyl, at position 4 are particularly preferred.

(0074)

While the racemic form of the transition metal compound (II-5) will generally be used as the catalyst component in this invention, the R-form or S-form can also be used. These transition metal compounds (II-5) can be synthesized by known methods from indene derivatives, for example, by the method described in Japanese Laid Open (Unexamined or Kokai or A) Patent Application Number Hei 4-268307 (268,307/1992).

(0075)

Compounds with the following formula (III-1) can also be used as the Group 4 transition metal compound (A)



wherein M^1 is a transition metal atom from Group 4 of the Periodic Table.

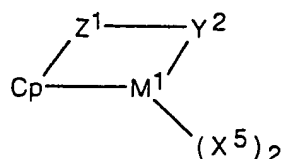
(0076)

Here, L^2 is the derivative of a delocalized π -bonding group and imparts a constrained geometric shape to the M^1 metal active site. The groups X^5 may be the same as each other or may differ from one another and represent the hydrogen atom, a halogen atom, or a hydrocarbyl, silyl, or germyl group containing no more than 20 carbon atoms, silicon atoms, or germanium atoms.

(0077)

Compounds with the following formula (III-2) are preferred among compounds with general formula (III-1).

(0078)



(III-2)

(0079)

M¹ in this formula is a transition metal atom from Group 4 of the Periodic Table and specifically is zirconium, titanium, or hafnium with zirconium being preferred. Cp is π -bonded to M¹ and represents a substituted cyclopentadienyl group bearing a substituent Z or a derivative of such a substituted cyclopentadienyl group.

(0080)

Z¹ is a ligand containing the oxygen atom, sulfur atom, boron atom, or an element from Group 14 of the Periodic Table and can be exemplified by $-\text{Si}(\text{R}^{55})_2-$, $-\text{C}(\text{R}^{55})_2-$, $-\text{Si}(\text{R}^{55})_2\text{Si}(\text{R}^{55})_2-$, $-\text{C}(\text{R}^{55})_2\text{C}(\text{R}^{55})_2-$, $-\text{C}(\text{R}^{55})_2\text{C}(\text{R}^{55})_2\text{C}(\text{R}^{55})_2-$, $-\text{C}(\text{R}^{55})=\text{C}(\text{R}^{55})-$, $-\text{C}(\text{R}^{55})_2\text{Si}(\text{R}^{55})_2-$, and $-\text{Ge}(\text{R}^{55})_2-$.

(0081)

Y² represents a ligand containing the nitrogen atom, phosphorus atom, oxygen atom, or sulfur atom and can be exemplified by $-\text{N}(\text{R}^{52})-$, $-\text{O}-$, $-\text{S}-$, and $-\text{P}(\text{R}^{52})-$. A condensed ring can also be formed by Z¹ and Y².

(0082)

R⁵⁵ is the hydrogen atom or a group that contains up to 20 non-hydrogen atoms and is selected from alkyl, aryl, silyl, halogenated alkyl, halogenated aryl, and their combinations. R⁵² is C₁ to C₁₀ alkyl, C₆ to C₁₀ aryl, or C₇ to C₁₀ aralkyl or together with one or more of the R⁵⁵ substituents can form a condensed ring system having up to 30 non-hydrogen atoms.

(0083)

Specific examples of the transition metal compound (III-2) are as follows:

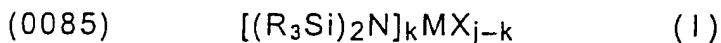
(tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediylzirconium dichloride,
 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium dichloride,
 (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediylzirconium dichloride,
 (methylamido)(tetramethyl- η^5 -cyclopentadienyl)-1,2-ethanediyltitanium dichloride,

(ethylamido)(tetramethyl- η^5 -cyclopentadienyl)methylenetitanium dichloride,
 (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride,
 (tert-butylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanezirconium dichloride,
 (benzylamido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanetitanium dichloride, and
 (phenylphosphido)dimethyl(tetramethyl- η^5 -cyclopentadienyl)silanedibenzylzirconium.

(0084)

(B) The transition metal amide compound

The transition metal amide compound (B) used by this invention is a transition metal amide compound with the following general formula (I) or (I-1).



M in the preceding formula represents a transition metal atom from Groups 3-6 of the Periodic Table and preferably is a Group 4 transition metal atom such as titanium, zirconium, or hafnium.

(0086)

j represents the valence of the transition metal atom M, while k is an integer from 1 to j. Each R is independently selected from hydrocarbyl and halogenated hydrocarbyl.

(0087)

The hydrocarbyl can be specifically exemplified by C₁ to C₂₀ straight-chain and branched alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, hexyl, octyl, decyl, and octadecyl; C₆ to C₂₀ aryl such as phenyl and naphthyl; substituted aryl as afforded by placing 1-5 substituents, e.g., C₁ to C₂₀ alkyl, on the aforementioned aryl groups; cycloalkyl such as cyclopentyl, cyclohexyl, norbornyl, and adamantyl; alkenyl such as vinyl, propenyl, and cyclohexenyl; and arylalkyl such as benzyl, phenylethyl, and phenylpropyl.

(0088)

The halogenated hydrocarbyl can be exemplified by groups afforded by substituting halogen into the aforementioned hydrocarbyl. The R groups can be connected to each other to form a ring, for example, an aliphatic ring. The R groups bonded to different nitrogen atoms can be the same as each other or may differ from one another.

(0089)

X represents the hydrogen atom, halogen atoms, C₁ to C₂₀ hydrocarbyl, C₁ to C₂₀ halogenated hydrocarbyl, oxygen-containing groups, sulfur-containing groups, and silicon-containing groups and can be specifically exemplified by the same atoms and groups provided above in the discussion of L in general formula (II-2). When j-k is ≥ 2 , the X's can be the same as each other or may differ from one another.

(0090)

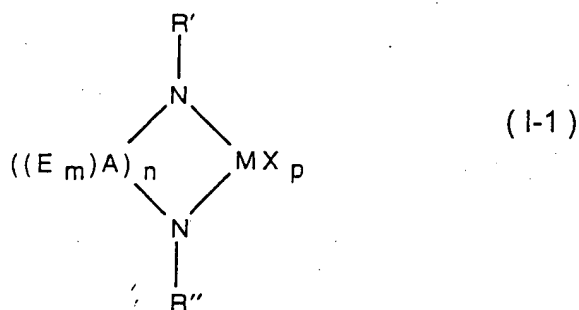
Among the preceding, halogen atoms, C₁ to C₂₀ hydrocarbyl, and sulfonate groups are preferred. Specific examples of the transition metal amide compound (I) are provided hereinbelow, but the transition metal amide compound (I) is not limited to the following.

[bis(trimethylsilyl)amido]titanium trichloride
bis[bis(triethylsilyl)amido]titanium dichloride
bis[bis(trimethylsilyl)amido]titanium dichloride
tris[bis(trimethylsilyl)amido]titanium chloride
tetrakis[bis(trimethylsilyl)amido]titanium
[bis(trimethylsilyl)amido]zirconium trichloride
bis[bis(triethylsilyl)amido]zirconium dichloride
bis[bis(trimethylsilyl)amido]zirconium dichloride
tris[bis(trimethylsilyl)amido]zirconium chloride
tetrakis[bis(trimethylsilyl)amido]zirconium
[bis(trimethylsilyl)amido]hafnium trichloride
bis[bis(triethylsilyl)amido]hafnium dichloride
bis[bis(trimethylsilyl)amido]hafnium dichloride
tris[bis(trimethylsilyl)amido]hafnium chloride
tetrakis[bis(trimethylsilyl)amido]hafnium

(0091)

The transition metal amide compound with general formula (I-1) is described in the following.

(0092)



(0093)

M in the preceding formula is the same as M described above for general formula (I) and is preferably a Group 4 transition metal atom such as titanium, zirconium, or hafnium with titanium being particularly preferred.

(0094)

R' and R'' are each independently selected from the hydrogen atom, hydrocarbyl, halogenated hydrocarbyl, organosilyl groups, and hydrocarbyl substituted by a substituent that contains at least one element selected from nitrogen, oxygen, phosphorus, sulfur, and silicon.

(0095)

The hydrocarbyl and halogenated hydrocarbyl can be specifically exemplified by the same hydrocarbyl and halogenated hydrocarbyl as given for R in the preceding discussion of general formula (I). The organosilyl groups can be specifically exemplified by methylsilyl, dimethylsilyl, trimethylsilyl, ethylsilyl, diethylsilyl, triethylsilyl, and triphenylsilyl.

(0096)

The hydrocarbyl substituted by a substituent that contains at least one element selected from nitrogen, oxygen, phosphorus, sulfur, and silicon can be exemplified by groups afforded by substituting $-\text{COOCH}_3$, $-\text{N}(\text{CH}_3)\text{C}(\text{O})\text{CH}_3$, $-\text{OC}(\text{O})\text{CH}_3$, $-\text{CN}$, $-\text{N}(\text{C}_2\text{H}_5)_2$, $-\text{N}(\text{CH}_3)\text{S}(\text{O}_2)\text{CH}_3$, or $-\text{P}(\text{C}_6\text{H}_5)_2$ into the aforementioned hydrocarbyl.

(0097)

m is an integer from 0 to 2 while n is an integer from 1 to 5. A represents an atom from Groups 13 to 16 of the Periodic Table and can be specifically exemplified by boron, carbon, nitrogen, oxygen, silicon, phosphorus, sulfur, germanium, selenium, and tin wherein carbon and silicon are preferred. The plurality of A's present when n is greater than or equal to 2 may

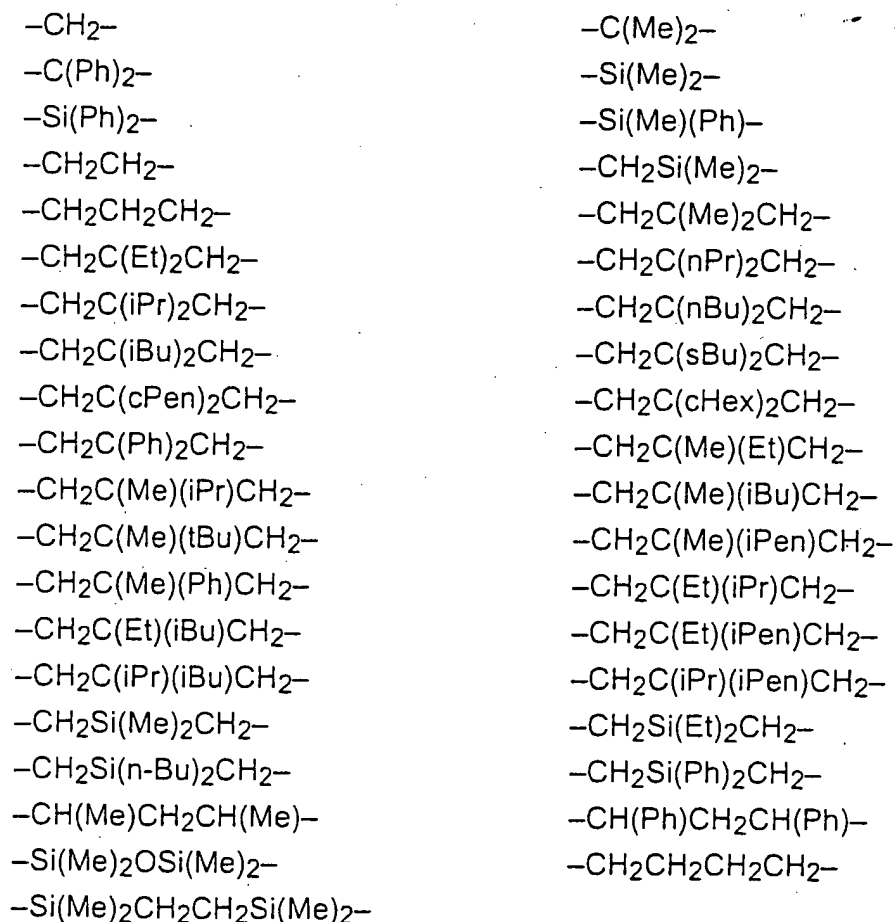
be the same as each other or may differ from one another.

(0098)

The group E is a substituent that contains at least one element selected from carbon, hydrogen, oxygen, halogen, nitrogen, sulfur, phosphorus, boron, and silicon. When a plurality of groups represented by E are present, said plurality of groups represented by E may be the same as each other or may differ from one another and two or more groups represented by E may be connected to each other to form a ring.

(0099)

The bridging group $-(E_m)A_n-$ that is bonded to the two nitrogen atoms can be specifically exemplified by the following groups.



(0105)

The following abbreviations are used in the preceding examples: Me for methyl, Et for ethyl, nPr for n-propyl, iPr for isopropyl, nBu for n-butyl, iBu for isobutyl, sBu for sec-butyl, t-Bu for tert-butyl, iPen for isopentyl, cPen for cyclopentyl, cHex for cyclohexyl, and Ph for phenyl.

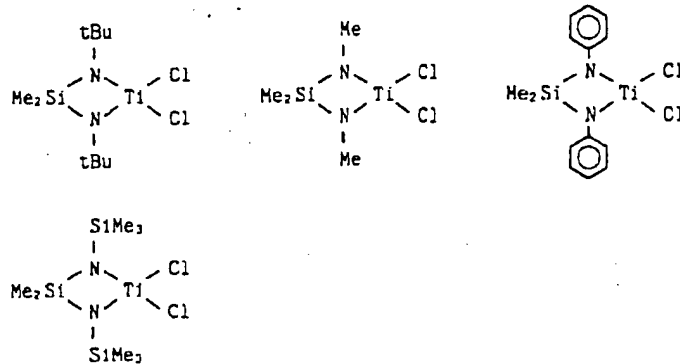
(0106)

p is an integer from 0 to 4. X represents the hydrogen atom, halogen atoms, C₁ to C₂₀ hydrocarbyl, C₁ to C₂₀ halogenated hydrocarbyl, an oxygen-containing group, a sulfur-containing group, or a silicon-containing group and is specifically exemplified as for L in the aforementioned general formula (II-1). When p ≥ 2, the plurality of groups represented by X may be the same as each other or may differ from one another.

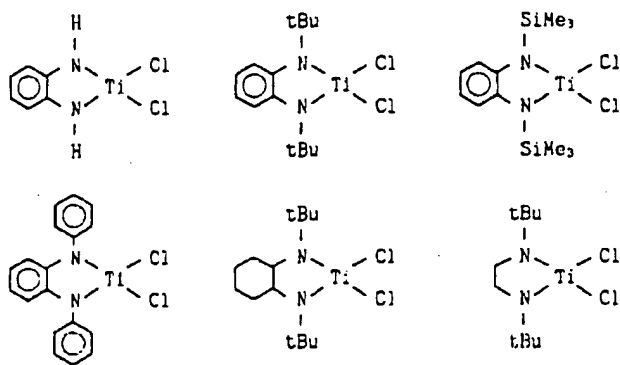
(0107)

Among the various possibilities, halogen atoms, C₁ to C₂₀ hydrocarbyl, and sulfonate groups are preferred. The transition metal amide compound (I-1) is specifically exemplified as follows, but is not limited to the following specific examples.

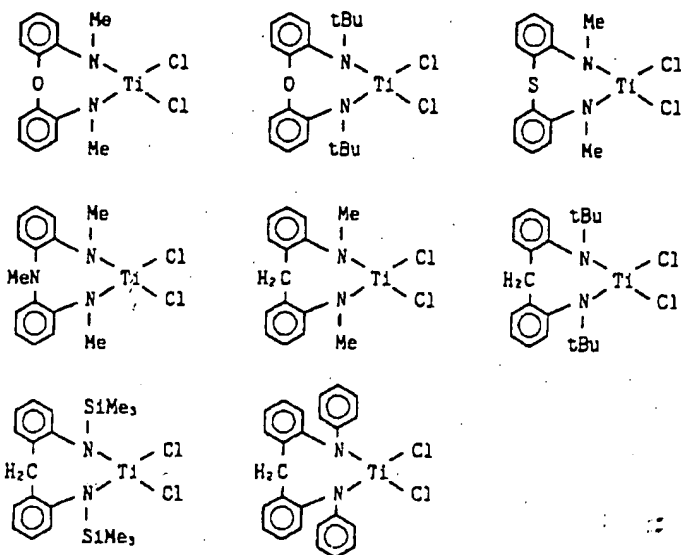
(0108)



(0109)



(0112)



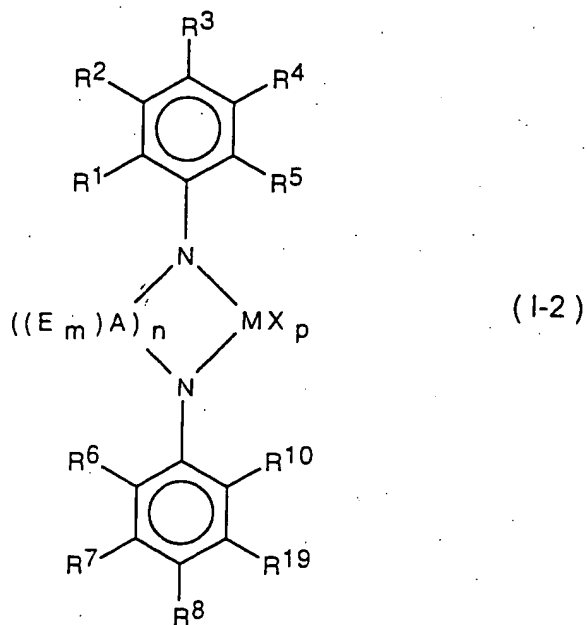
(0113)

The following abbreviations are used in the preceding examples: Me for methyl, Et for ethyl, iPr for isopropyl, and tBu for tert-butyl. This invention can also use transition metal amide compounds generated by replacing the titanium in the preceding compounds with zirconium or hafnium.

(0114)

Among transition metal amide compounds with general formula (I-1), the use is preferred in the present invention of transition metal amide compounds with general formula (I-2) in which R' and R'' are substituted aryl bearing from 1-5 substituents such as alkyl.

(0115)



(0116)

M in the preceding formula is the same as M in general formula (I) and is preferably a Group 4 transition metal atom such as titanium, zirconium, or hafnium and particularly preferably is titanium.

(0117)

Each of R^1 to R^{10} is independently selected from the hydrogen atom, halogen atoms, hydrocarbyl, halogenated hydrocarbyl, organosilyl groups, alkoxy groups, aryloxy groups, $-\text{COOR}^{11}$, $-\text{N}(\text{R}^{12})\text{C}(\text{O})\text{R}^{13}$, $-\text{OC}(\text{O})\text{R}^{14}$, $-\text{CN}$, $-\text{NR}^{15}_2$, and $-\text{N}(\text{R}^{16})\text{S}(\text{O}_2)\text{R}^{17}$ wherein R^{11} to R^{17} represent C_1 to C_5 alkyl, with the provisos that at least one of R^1 to R^5 is not hydrogen and at least one of R^6 to R^{10} is not hydrogen.

(0118)

The halogen atoms are the same as for X in general formula (I), while the hydrocarbyl, halogenated hydrocarbyl, and organosilyl groups are the same as for R' and R'' in general formula (I-1).

(0119)

The alkoxy can be specifically exemplified by methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, and tert-butoxy. The aryloxy can be specifically exemplified by phenoxy,

2,6-dimethylphenoxy, and 2,4,6-trimethylphenoxy.

(0120)

The groups represented by $-\text{COOR}^{11}$, $-\text{N(R}^{12})\text{C(O)R}^{13}$, $-\text{OC(O)R}^{14}$, $-\text{CN}$, $-\text{NR}^{15}_2$, and $-\text{N(R}^{16})\text{S(O}_2\text{)R}^{17}$ (wherein R^{11} to R^{17} represent C_1 to C_5 alkyl) can be exemplified by $-\text{COOCH}_3$, $-\text{N(CH}_3\text{)C(O)CH}_3$, $-\text{OC(O)CH}_3$, $-\text{CN}$, $-\text{N(C}_2\text{H}_5\text{)}_2$, and $-\text{N(CH}_3\text{)S(O}_2\text{)CH}_3$.

(0121)

Two or more — preferably adjacent — groups among the groups R^1 to R^5 may be interconnected to form a ring (e.g., an aromatic ring, aliphatic ring) together with the carbon atoms to which they are respectively bonded. Two or more — preferably adjacent — groups among the groups R^6 to R^{10} may be interconnected to form a ring (e.g., an aromatic ring, aliphatic ring) together with the carbon atoms to which they are respectively bonded.

(0122)

m is an integer from 0 to 2, while n is an integer from 1 to 5. The substituent A is the same as A in the preceding general formula (I-1) and is preferably a carbon atom or silicon atom. When $n \geq 2$, the plurality of A 's may be the same as each other or may differ from one another.

(0123)

The group E is the same as E in the preceding general formula (I-1) and is preferably a substituent that contains at least one element selected from carbon, hydrogen, nitrogen, and silicon. When a plurality of groups represented by E are present said plurality of groups represented by E may be the same as each other or may differ from one another and two or more groups represented by E may be connected to each other to form a ring.

(0124)

The bridging group $-(\text{E}_m\text{A})_n-$ that is bonded to the two nitrogen atoms can be specifically exemplified by the same groups as provided above. p is an integer from 0 to 4.

(0125)

X represents the hydrogen atom, a halogen atom, C_1 to C_{20} hydrocarbyl, C_1 to C_{20} halogenated hydrocarbyl, an oxygen-containing group, or a sulfur-containing group and is specifically exemplified as for L in general formula (II-1).

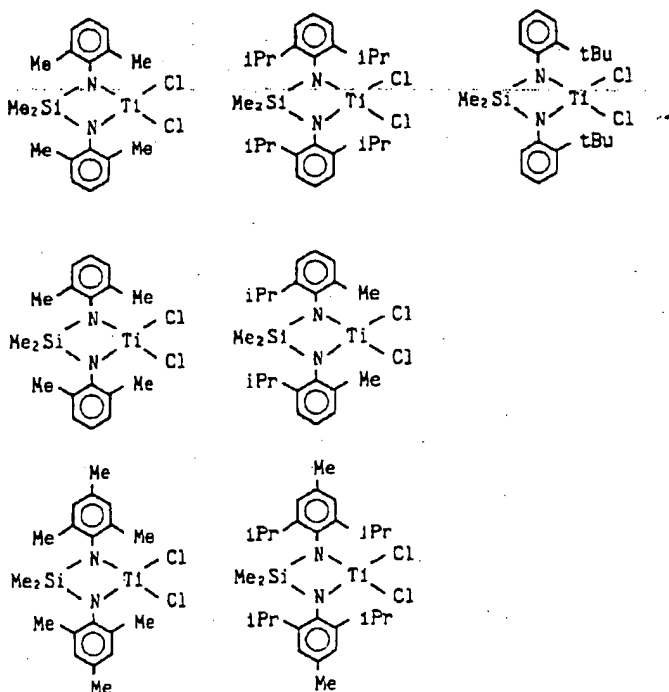
(0126)

Preferred among these are halogen atoms, C₁ to C₂₀ hydrocarbyl, and sulfonate groups. When $p \geq 2$, the plurality of groups represented by X may be the same as each other or may differ from one another.

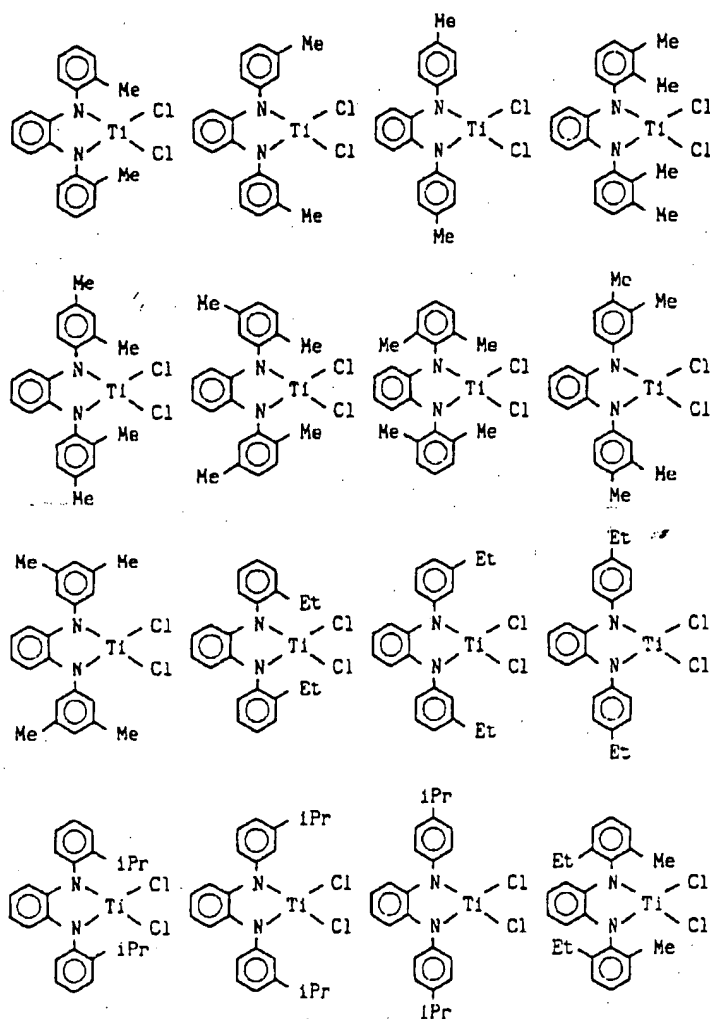
(0127)

The transition metal amide compound (I-2) is specifically exemplified as follows, but is not limited to the following specific examples.

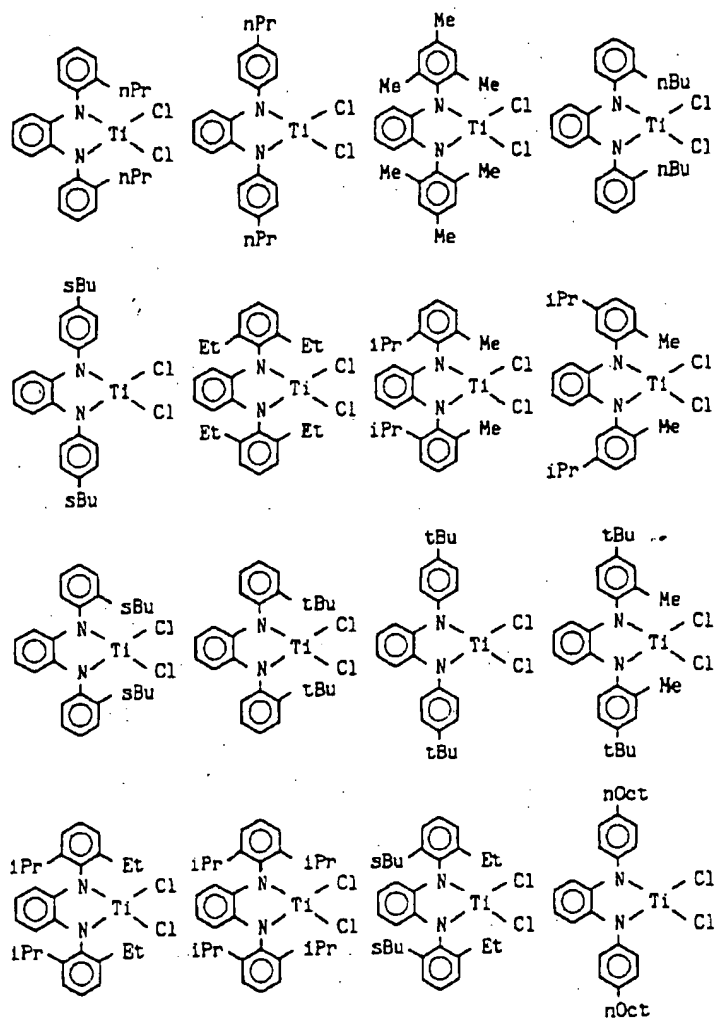
(0128)



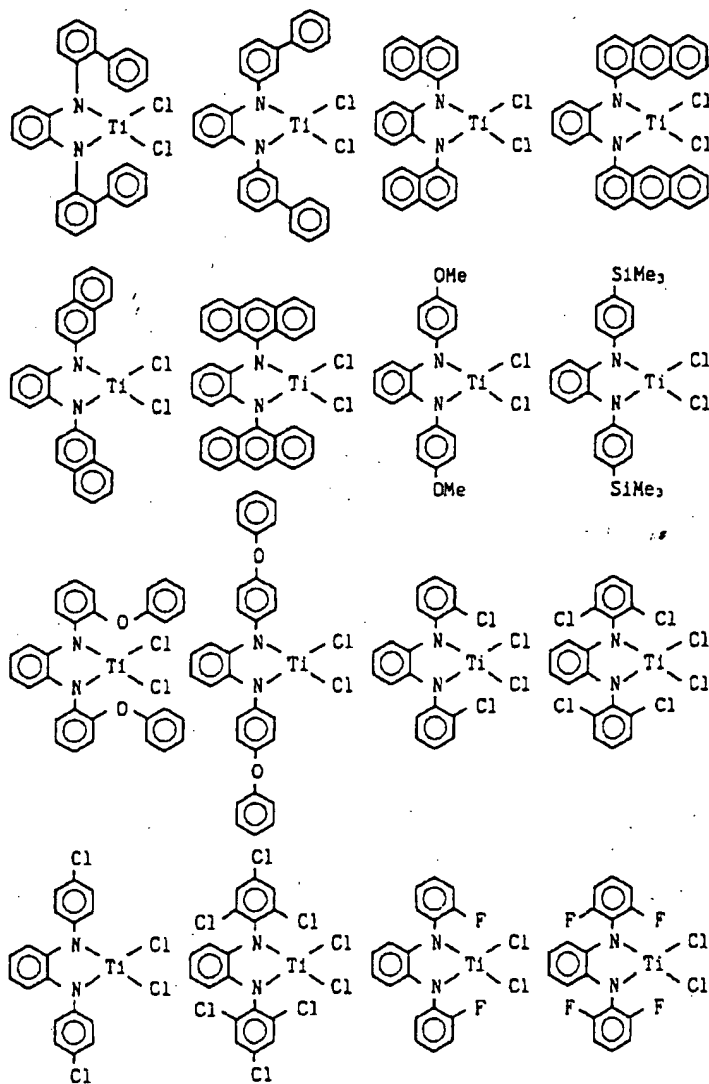
(0129)



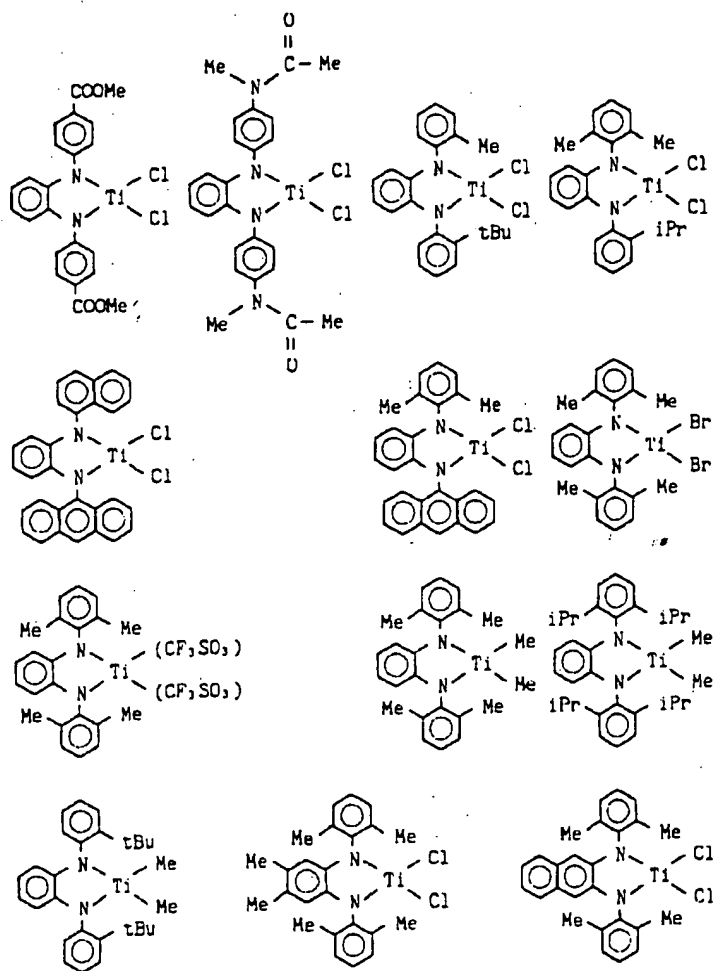
(0130)



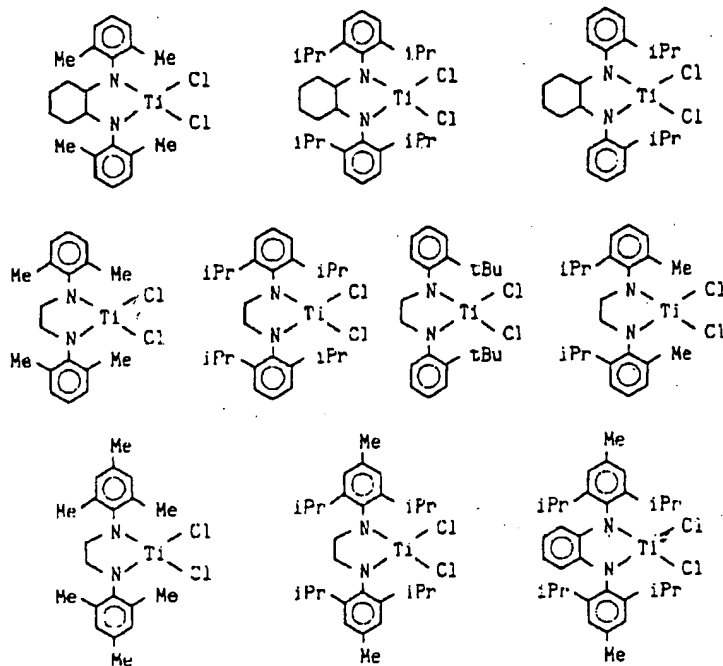
(0131)



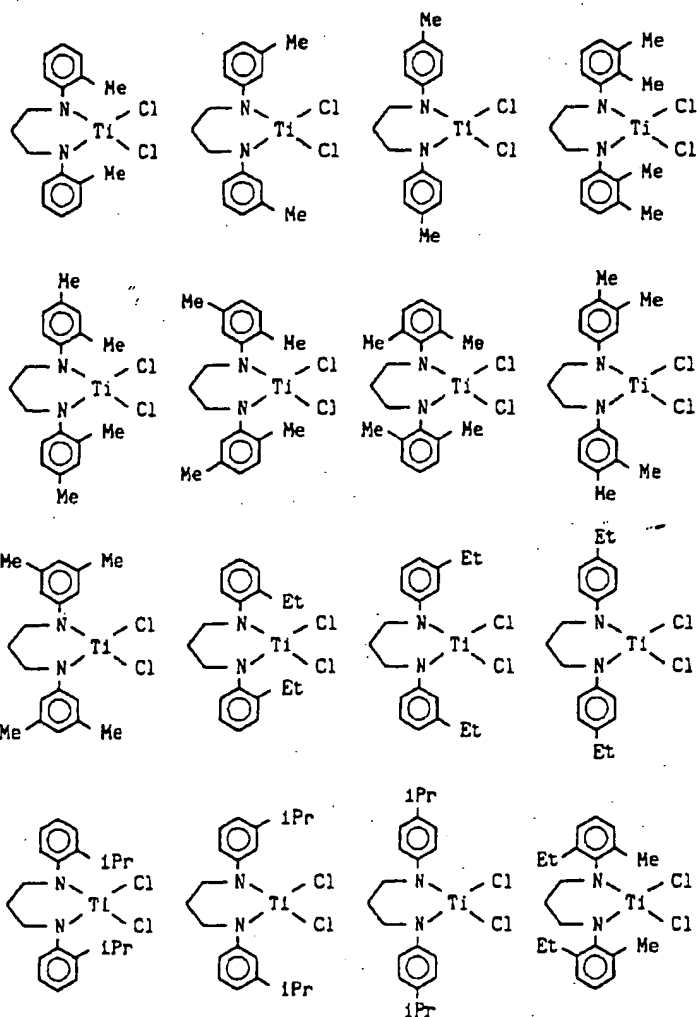
(0132)



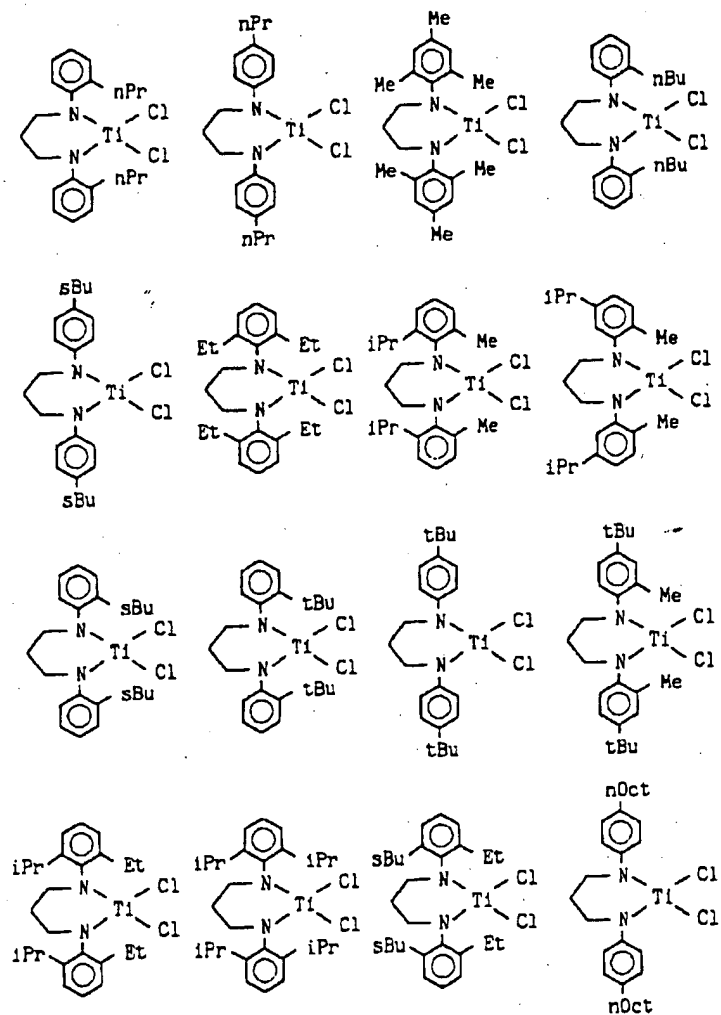
(0133)



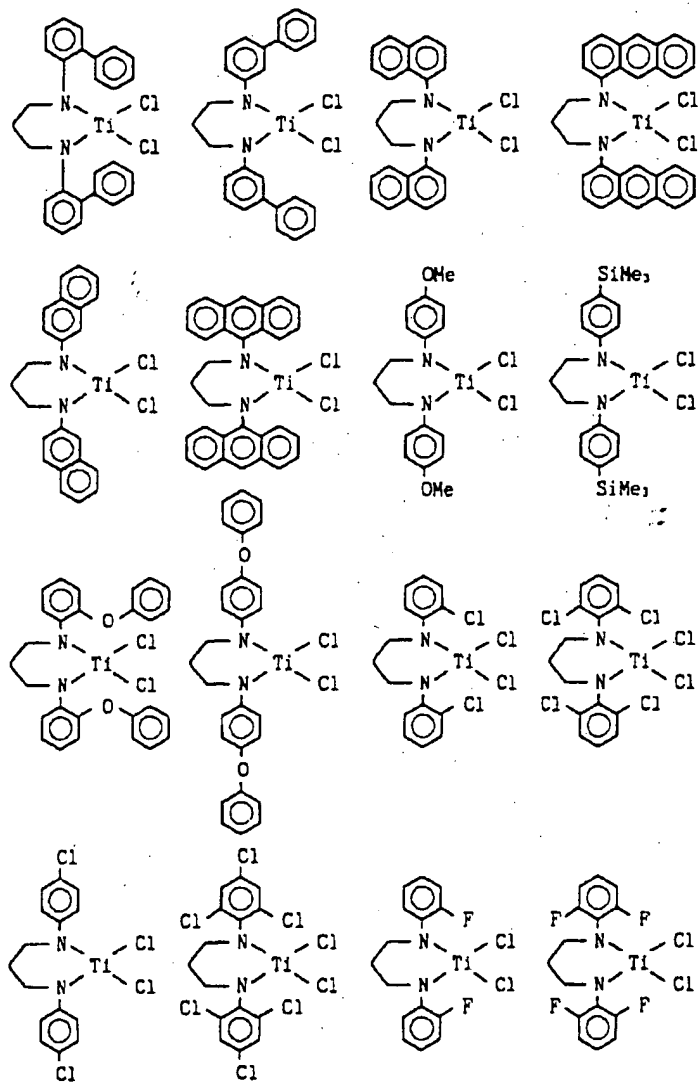
(0134)



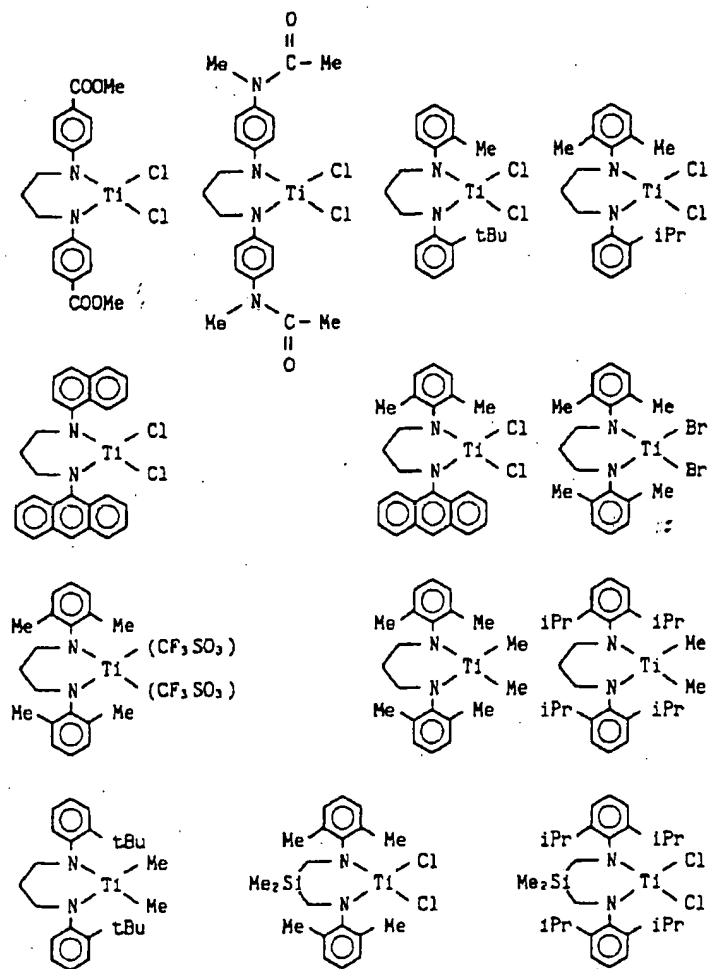
(0135)



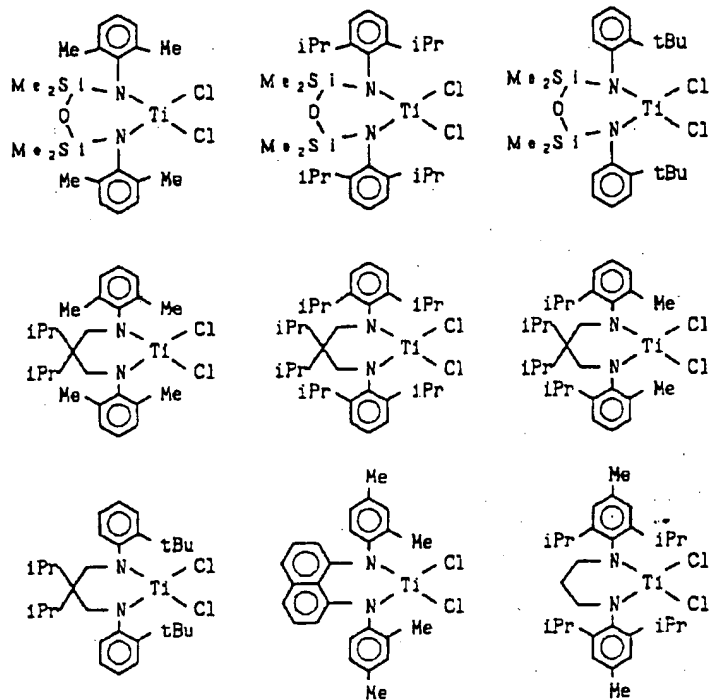
(0136)



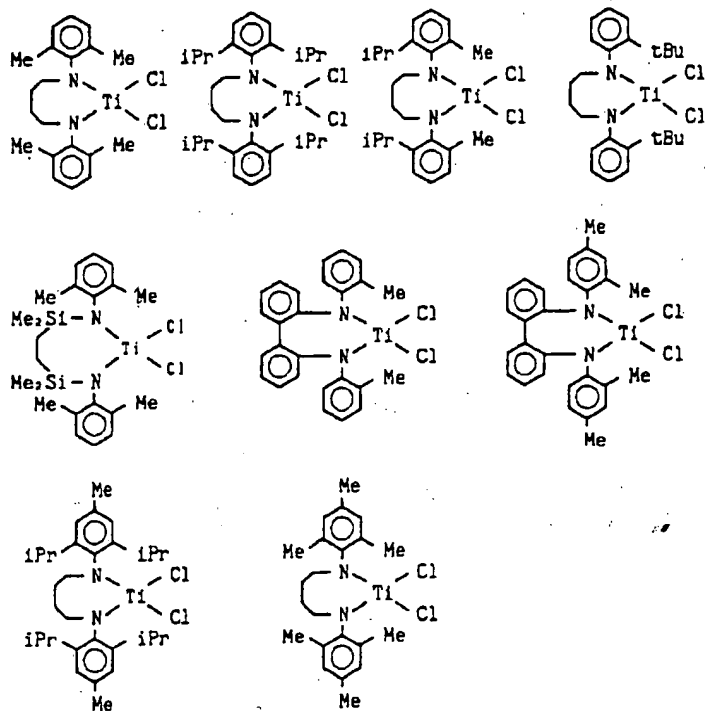
(0137)



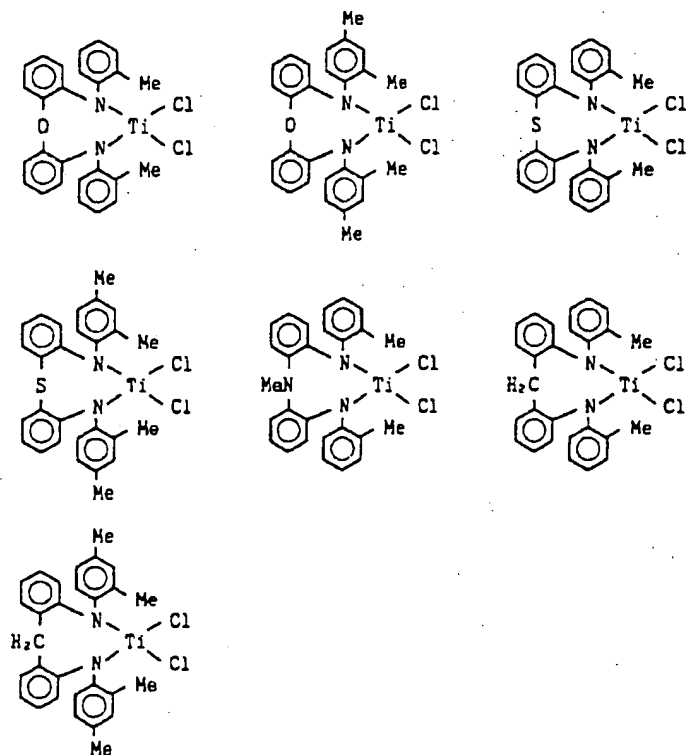
(0138)



(0139)



(0140)



(0141)

The following abbreviations are used in the preceding examples: Me for methyl, Et for ethyl, iPr for isopropyl, nPr for n-propyl, nBu for n-butyl, sBu for sec-butyl, t-Bu for tert-butyl, and nOct for n-octyl.

(0142)

This invention can also use transition metal amide compounds as afforded by replacing the titanium in the preceding compounds with zirconium or hafnium. Among the transition metal amide compounds under consideration, in preferred transition metal amide compounds M = titanium, A in the group bonded to the two nitrogen atoms is carbon or silicon, and n is 2 or 3.

(0143)

Among the transition metal amide compounds under consideration, in preferred transition metal amide compounds M = titanium, A in the group bonded to the two nitrogen atoms is carbon or silicon, and n is 2 or 3.²

(0144)

Among transition metal amide compounds with general formulas (I) and (I-1), transition metal amide compounds with general formula (I-1) are preferably used, and among these the use of transition metal amide compounds with general formula (I-2) is particularly preferred.

(0145)

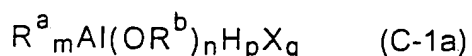
The preceding compounds can be used singly or in combinations of two or more.

(C-1) The organometal compounds

Organometal compounds from Groups 1 and 2 and 12 and 13 as specifically defined below can be used as the organometal compound (C-1) employed in the present invention.

(0146)

Organoaluminum compounds with the general formula



² Translator's Note. This sentence comprising section (0143) is in fact identical to the second sentence in section (0142) in the Japanese source document.

in which R^a and R^b are independently selected from C_1 to C_{15} and preferably C_1 to C_4 hydrocarbyl; X is a halogen atom; and $0 < m \leq 3$, $0 \leq n < 3$, $0 \leq p < 3$, $0 \leq q < 3$, and $m + n + p + q = 3$.

(0147)

The complex alkylates of aluminum and a Group 1 metal with the general formula



in which M^2 is Li, Na, or K and R^a is C_1 to C_{15} and preferably C_1 to C_4 hydrocarbyl.

(0148)

The dialkylates of a Group 2 or Group 12 metal with the general formula

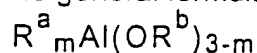


in which R^a and R^b are independently selected from C_1 to C_{15} and preferably C_1 to C_4 hydrocarbyl and M^3 is Mg, Zn, or Cd.

(0149)

The organoaluminum compounds encompassed by (C-1a) can be exemplified by the following compounds:

organoaluminum compounds with the general formula



in which R^a and R^b are independently selected from C_1 to C_{15} and preferably C_1 to C_4 hydrocarbyl and m is preferably a number satisfying $1.5 \leq m \leq 3$;

organoaluminum compounds with the general formula



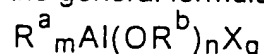
in which R^a is C_1 to C_{15} and preferably C_1 to C_4 hydrocarbyl, X is halogen, and m preferably satisfies $0 < m < 3$;

organoaluminum compounds with the general formula



in which R^a is C_1 to C_{15} and preferably C_1 to C_4 hydrocarbyl and m preferably satisfies $2 \leq m < 3$; and

organoaluminum compounds with the general formula



in which R^a and R^b are independently selected from C_1 to C_{15} and preferably C_1 to C_4 hydrocarbyl, X is a halogen atom, and $0 < m \leq 3$, $0 \leq n < 3$, $0 \leq q < 3$, and $m + n + q = 3$.

(0150)

The aluminum compounds encompassed by (C-1a) can be more specifically exemplified by tri-n-alkylaluminums such as triethylaluminum and tri-n-butylaluminum;

tri-branched chain-alkylaluminums such as triisopropylaluminum, triisobutylaluminum, tri-sec-butylaluminum, tri-tert-butylaluminum, tri-2-methylbutylaluminum, tri-3-methylbutylaluminum, tri-2-methylpentylaluminum, tri-3-methylpentylaluminum, tri-4-methylpentylaluminum, tri-2-methylhexylaluminum, tri-3-methylhexylaluminum, and tri-2-ethylhexylaluminum;

tricycloalkylaluminums such as tricyclohexylaluminum;

triarylaluminums such as triphenylaluminum and tritolylaluminum;

dialkylaluminum hydrides such as diisobutylaluminum hydride;

trialkenylaluminums such as triisoprenylaluminum;

alkylaluminum alkoxides such as isobutylaluminum methoxide, isobutylaluminum ethoxide, and isobutylaluminum isopropoxide;

dialkylaluminum alkoxides such as diethylaluminum ethoxide and dibutylaluminum butoxide;

alkylaluminum sesquialkoxides such as ethylaluminum sesquiethoxide and butylaluminum sesquibutoxide;

partially alkoxyated alkylaluminums with the average compositional formula $R^a_{2.5} Al(OR^b)_{0.5}$;

alkylaluminum aryloxides such as diethylaluminum (2,6-di-t-butyl-4-methylphenoxide), ethylaluminum bis(2,6-di-t-butyl-4-methylphenoxide), diisobutylaluminum (2,6-di-t-butyl-4-methylphenoxide), and isobutylaluminum bis(2,6-di-t-butyl-4-methylphenoxide);

dialkylaluminum halides such as diethylaluminum chloride, dibutylaluminum chloride, and diethylaluminum bromide;

alkylaluminum sesquihalides such as ethylaluminum sesquichloride, butylaluminum sesquichloride, and ethylaluminum sesquibromide;

partially halogenated alkylaluminums such as alkylaluminum dihalides such as ethylaluminum dichloride, propylaluminum dichloride, and butylaluminum dibromide;

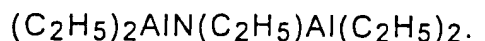
dialkylaluminum hydrides such as diethylaluminum hydride and dibutylaluminum hydride;

other partial hydrogenated alkylaluminums such as alkylaluminum dihydrides such as ethylaluminum dihydride and propylaluminum dihydride; and

partially alkoxyated and halogenated alkylaluminums such as ethylaluminum ethoxychloride, butylaluminum butoxychloride, and ethylaluminum ethoxybromide.

(0151)

Also usable are compounds that resemble (C-1a), for example, organoaluminum compounds as afforded by bonding two or more aluminum compounds to each other through the nitrogen atom. Compounds of this type can be specifically exemplified by



(0152)

Compounds encompassed by (C-1b) can be exemplified by $\text{LiAl}(\text{C}_2\text{H}_5)_4$ and $\text{LiAl}(\text{C}_7\text{H}_{15})_4$.

(0153)

In addition to the preceding, isoprenylaluminums with the following general formula can also be used as the organometal compound (C-1)



wherein x , y , and z are positive numbers and $z \geq 2x$.

(0154)

In addition to the preceding, the following can also be used as the organometal compound (C-1): methyllithium, ethyllithium, propyllithium, butyllithium, methylmagnesium bromide, methylmagnesium chloride, ethylmagnesium bromide, ethylmagnesium chloride, propylmagnesium bromide, propylmagnesium chloride, butylmagnesium bromide, butylmagnesium chloride, dimethylmagnesium, diethylmagnesium, dibutylmagnesium, and butylethylmagnesium.

(0155)

Compounds that will form the above-described organoaluminum compounds in the polymerization system can also be used, for example, the combination of aluminum halide and alkylolithium and the combination of aluminum halide and alkylmagnesium.

(0156)

Organoaluminum compounds are preferred among the preceding. The above-described organometal compound (C-1) may be a single compound or a combination of two or more compounds.

(0157)

(C-2) The organoaluminumoxy compounds

The organoaluminumoxy compound (C-2) used by the present invention may be an aluminoxane as known in the art or a benzene-insoluble organoaluminumoxy compound as exemplified in Japanese Laid Open (Unexamined or Kokai or A) Patent Application Number Hei 2-78687 (78,687/1990).

(0158)

The above-referenced aluminoxanes as known in the art can be synthesized, for example, by the following methods and will generally be obtained as a solution in hydrocarbon solvent.

- (1) Reaction of an organoaluminum compound with water of adsorption or crystallization by the addition of an organoaluminum compound, e.g., trialkylaluminum, to a suspension in hydrocarbon medium of a compound containing water of adsorption or a salt containing water of crystallization, for example, magnesium chloride hydrate, copper sulfate hydrate, aluminum sulfate hydrate, nickel sulfate hydrate, and cerous chloride hydrate.
- (2) The direct action of water, ice, or water vapor on an organoaluminum compound, e.g., trialkylaluminum, in a medium such as benzene, toluene, ethyl ether, or tetrahydrofuran.
- (3) The reaction of an organotin oxide, e.g., dimethyltin oxide or dibutyltin oxide, with an organoaluminum compound, e.g., trialkylaluminum, in a medium such as decane, benzene, or toluene.

(0159)

This aluminoxane may contain small amounts of organometal component. In addition, after the solvent or unreacted organoaluminum compound has been distilled from the above-described aluminoxane solutions, the aluminoxane may be redissolved in solvent or suspended in a poor solvent for the aluminoxane.

(0160)

The organoaluminum compounds used in aluminoxane synthesis can be specifically exemplified by the same organoaluminum compounds provided above as examples of the

organoaluminum compounds encompassed by (C-1).

(0161)

Trialkylaluminums and tricycloalkylaluminums are preferred among the preceding, with trimethylaluminum being particularly preferred. The subject organoaluminum compound may be a single compound or a combination of two or more compounds.

(0162)

The solvent used in aluminoxane synthesis can be exemplified by hydrocarbon solvents, for example, aromatic hydrocarbons such as benzene, toluene, xylene, cumene, and cymene; aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decane, dodecane, hexadecane, and octadecane; alicyclic hydrocarbons such as cyclopentane, cyclohexane, cyclooctane, and methylcyclopentane; petroleum distillates such as gasoline, kerosene, and light oil; and the halogenated derivatives, and particularly the chlorinated derivatives and brominated derivatives, of the above-listed aromatic hydrocarbons, aliphatic hydrocarbons, and alicyclic hydrocarbons. Ethers such as ethyl ether and tetrahydrofuran can also be used. Aromatic hydrocarbons and aliphatic hydrocarbons are particularly preferred among the solvents listed above.

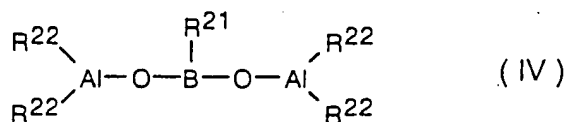
(0163)

The benzene-insoluble organoaluminumoxy compounds used in the present invention should be either insoluble or sparingly soluble in benzene, i.e., the Al component dissolving in 60°C benzene should generally be $\leq 10\%$ and is preferably $\leq 5\%$ and particularly preferably is $\leq 2\%$, in each case as Al atoms.

(0164)

The organoaluminumoxy compound used by the present invention can also be a boron-containing organoaluminumoxy compound as defined by general formula (IV)

(0165)



(0166)

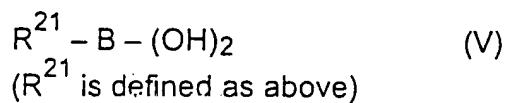
wherein:

R^{21} represents C_1 to C_{10} hydrocarbyl and

each R^{22} is independently selected from the hydrogen atom, halogen atoms, and C_1 to C_{10} hydrocarbyl.

(0167)

This boron-containing organoaluminumoxy compound (IV) can be synthesized by reacting an organoaluminum compound and an alkylboronic acid with general formula (V)



for 1 minute to 24 hours at -80°C to room temperature in an inert solvent under an inert gas blanket.

(0168)

The alkylboronic acid (V) can be specifically exemplified by methylboronic acid, ethylboronic acid, isopropylboronic acid, n-propylboronic acid, n-butylboronic acid, isobutylboronic acid, n-hexylboronic acid, cyclohexylboronic acid, phenylboronic acid, 3,5-difluoro[phenyl]boronic acid, pentafluorophenylboronic acid, and 3,5-bis(trifluoromethyl)phenylboronic acid. Preferred among the foregoing are methylboronic acid, n-butylboronic acid, isobutylboronic acid, 3,5-difluorophenylboronic acid, and pentafluorophenylboronic acid. These can be used singly or in combinations of two or more selections.

(0169)

The organoaluminum compound reacted with the alkylboronic acid can be specifically exemplified by the same organoaluminum compounds provided above as examples of the organoaluminum compounds encompassed by (C-1).

(0170)

Preferred among the foregoing organoaluminum compounds are trialkylaluminums and tricycloalkylaluminums with trimethylaluminum, triethylaluminum, and triisobutylaluminum being particularly preferred. These can be used singly or in combinations of two or more selections.

(0171)

The organoaluminumoxy compound (C-2) under consideration can itself be used singly or in combinations of two or more selections.

(C-3) Compounds capable of reacting with the transition metal compound or transition metal amide compound to form an ion pair

The compound (C-3) used in this invention that is capable of reacting with the transition metal compound (A) or transition metal amide compound (B) to form an ion pair (compound (C-3) is referred to below as an ionizing ionic compound) can be exemplified by the Lewis acids, ionic compounds, borane compounds, and carborane compounds that are disclosed, for example, in Japanese Patent Application (PCT) Numbers Hei 1-501950 (501,950/1989) and Hei 1-502036 (502,036/1989); Japanese Laid Open (Unexamined or Kokai or A) Patent Application Numbers Hei 3-179005 (179,005/1991), Hei 3-179006 (179,006/1991), Hei 3-207703 (207,703/1991), and Hei 3-207704 (207,704/1991); and United States Patent 5,321,106.

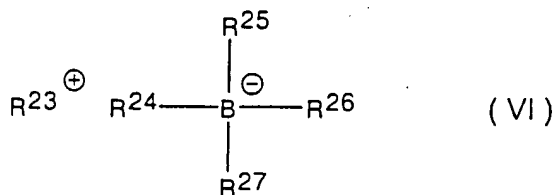
(0172)

The Lewis acids can be specifically exemplified by BR_3 compounds in which R = fluorine or the phenyl group wherein the latter may be substituted by the fluorine atom, methyl group, or trifluoromethyl group. These BR_3 compounds can be specifically exemplified by trifluoroboron, triphenylboron, tris(4-fluorophenyl)boron, tris(3,5-difluorophenyl)boron, tris(4-fluoromethylphenyl)boron, tris(pentafluorophenyl)boron, tris(p-tolyl)boron, tris(o-tolyl)boron, and tris(3,5-dimethylphenyl)boron.

(0173)

The ionic compounds can be exemplified by compounds with the following general formula (VI).

(0174)



(0175)

R^{23} in the preceding formula can be, for example, H^+ , carbonium cations, oxonium cations, ammonium cations, phosphonium cations, the cycloheptyltrienyl cation, and transition metal-containing ferrocenium cations.

(0176)

R^{24} to R^{27} can be independently selected from organic groups and are preferably selected from aryl and substituted aryl groups. The aforementioned carbonium cations can be specifically exemplified by trisubstituted carbonium cations such as the triphenylcarbonium cation, the tri(methylphenyl)carbonium cation, and the tri(dimethylphenyl)carbonium cation.

(0177)

The aforementioned ammonium cations can be specifically exemplified by trialkylammonium cations such as the trimethylammonium cation, the triethylammonium cation, the tripropylammonium cation, the tributylammonium cation, and the tri(n-butyl)ammonium cation; by N,N-dialkylanilinium cations such as the N,N-dimethylanilinium cation, the N,N-diethylanilinium cation, and the N,N-2,4,6-pentamethylanilinium cation; and by dialkylammonium cations such as the di(isopropyl)ammonium cation and the dicyclohexylammonium cation.

(0178)

The aforementioned phosphonium cations can be specifically exemplified by triarylphosphonium cations such as the triphenylphosphonium cation, the tri(methylphenyl)phosphonium cation, and the tri(dimethylphenyl)phosphonium cation.

(0179)

Carbonium cations and ammonium cations are preferred for R^{23} , while the triphenylcarbonium cation, N,N-dimethylanilinium cation, and N,N-diethylanilinium cation are specifically preferred.

(0180)

Also usable as the ionic compound are trialkyl-substituted ammonium salts, N,N-dialkylanilinium salts, dialkylammonium salts, and triarylphosphonium salts.

(0181)

The trialkyl-substituted ammonium salts can be specifically exemplified by
triethylammonium tetra(phenyl)boron,
tripropylammonium tetra(phenyl)boron,

tri(n-butyl)ammonium tetra(phenyl)boron,
 trimethylammonium tetra(p-tolyl)boron,
 trimethylammonium tetra(o-tolyl)boron,
 tri(n-butyl)butylammonium tetra(pentafluorophenyl)boron,
 tripropylammonium tetra(o,p-dimethylphenyl)boron,
 tri(n-butyl)ammonium tetra(m,m-dimethylphenyl)boron,
 tri(n-butyl)ammonium tetra(p-trifluoromethylphenyl)boron,
 tri(n-butyl)ammonium tetra(3,5-ditrifluoromethylphenyl)boron, and
 tri(n-butyl)ammonium tetra(o-tolyl)boron.

(0182)

The N,N-dialkylanilinium salts can be specifically exemplified by
 N,N-dimethylanilinium tetra(phenyl)boron,
 N,N-diethylanilinium tetra(phenyl)boron, and
 N,N-2,4,6-pentamethylanilinium tetra(phenyl)boron.

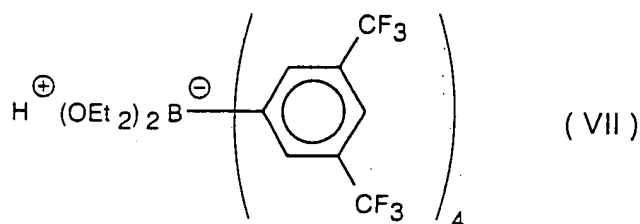
(0183)

The dialkylammonium salts can be specifically exemplified by
 di(1-propyl)ammonium tetra(pentafluorophenyl)boron and
 dicyclohexylammonium tetra(phenyl)boron.

(0184)

The ionic compounds can also be exemplified by triphenylcarbenium
 tetrakis(pentafluorophenyl)borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
 ferrocenium tetra(pentafluorophenyl)borate, triphenylcarbenium pentaphenylcyclopentadienyl
 complex, N,N-diethylanilinium pentaphenylcyclopentadienyl complex, and boron compounds
 with the following formulas (VII) and (VIII).

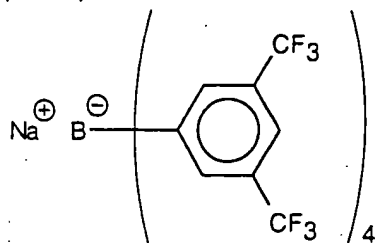
(0185)



(0186)

(Et = ethyl in the preceding formula)

(0187)



(VIII)

(0188)

The borane compounds can be specifically exemplified by
decaborane (14);

anion salts such as

bis[tri(n-butyl)ammonium] nonaborate,
bis[tri(n-butyl)ammonium] decaborate,
bis[tri(n-butyl)ammonium] undecaborate,
bis[tri(n-butyl)ammonium] dodecaborate,
bis[tri(n-butyl)ammonium] decachlorododecaborate, and
bis[tri(n-butyl)ammonium] dodecachlorododecaborate; and

salts of metal borane anions such as

tri(n-butyl)ammonium bis(dodecahydridododecaborate)cobaltate (III) and
bis[tri(n-butyl)ammonium] bis(dodecahydridododecaborate)nickelate (III).

(0189)

The carborane compounds can be specifically exemplified by

4-carbanonaborane (14),
1,3-dicarbanonaborane (13),
6,9-dicarbadeccaborane (14),
dodecahydrido-1-phenyl-1,3-dicarbanonaborane,
dodecahydrido-1-methyl-1,3-dicarbanonaborane,
undecahydrido-1,3-dimethyl-1,3-dicarbanonaborane,
7,8-dicarbaundecaborane (13),
2,7-dicarbaundecaborane (13),
undecahydrido-7,8-dimethyl-7,8-dicarbaundecaborane, and
dodecahydrido-11-methyl-2,7-dicarbaundecaborane;

anion salts such as

tri(n-butyl)ammonium 1-carbadecaborate,
tri(n-butyl)ammonium 1-carbaundecaborate,

tri(n-butyl)ammonium 1-carbadodecaborate,
 tri(n-butyl)ammonium 1-trimethylsilyl-1-carbadecaborate,
 tri(n-butyl)ammonium bromo-1-carbadodecaborate,
 tri(n-butyl)ammonium 6-carbadecaborate (14),
 tri(n-butyl)ammonium 6-carbadecaborate (12),
 tri(n-butyl)ammonium 7-carbaundecaborate (13),
 tri(n-butyl)ammonium 7,8-dicarbaundecaborate (12),
 tri(n-butyl)ammonium 2,9-dicarbaundecaborate (12),
 tri(n-butyl)ammonium dodecahydrido-8-methyl-7,9-dicarbaundecaborate,
 tri(n-butyl)ammonium undecahydrido-8-ethyl-7,9-dicarbaundecaborate,
 tri(n-butyl)ammonium undecahydrido-8-butyl-7,9-dicarbaundecaborate,
 tri(n-butyl)ammonium undecahydrido-8-allyl-7,9-dicarbaundecaborate,
 tri(n-butyl)ammonium undecahydrido-9-trimethylsilyl-7,8-dicarbaundecaborate, and
 tri(n-butyl)ammonium undecahydrido-4,6-dibromo-7-carbaundecaborate; and

the salts of metal carborane anions such as

tri(n-butyl)ammonium bis(nonahydrido-1,3-dicarbano-
 borate)cobaltate (III),
 tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundeca-
 borate)ferrate (III),
 tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundeca-
 borate)cobaltate (III),
 tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundeca-
 borate)nickelate (III),
 tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundeca-
 borate)cuprate (III),
 tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundeca-
 borate)aurate (III),
 tri(n-butyl)ammonium bis(nonahydrido-7,8-dimethyl-7,8-dicarbaundeca-
 borate)ferrate (III),
 tri(n-butyl)ammonium bis(nonahydrido-7,8-dimethyl-7,8-dicarbaundeca-
 borate)chromate (III),
 tri(n-butyl)ammonium bis(tribromooctahydrido-7,8-dicarbaundeca-
 borate)cobaltate (III),
 tris[tri(n-butyl)ammonium] bis(undecahydrido-7-carbaundecaborate)chromate (III),
 bis[tri(n-butyl)ammonium] bis(undecahydrido-7-carbaundeca-
 borate)manganate (IV),

bis[tri(n-butyl)ammonium] bis(undecahydrido-7-carbaundecaborate)cobaltate (III), and
bis[tri(n-butyl)ammonium] bis(undecahydrido-7-carbaundecaborate)nickelate (IV).

(0190)

These ionizing ionic compounds (C-3) may be used singly or in combinations of two or more. The olefin polymerization catalyst according to the present invention may also employ a microparticulate carrier (D) as described below on an optional basis in addition to the above-described (A) Group 4 transition metal compound, (B) transition metal amide compound, and (C) at least 1 compound selected from (C-1) organometal compounds, (C-2) organoaluminumoxy compounds, and (C-3) ionizing ionic compounds.

(0191)

(D) Microparticulate carriers

The microparticulate carrier (D) used on an optional basis by the present invention may be an inorganic or organic compound. Granular or microparticulate solids with a size of 10 to 300 μm and preferably 20 to 200 μm can be used for component (D). Porous oxides are preferred for the inorganic compounds and may be specifically exemplified by SiO_2 , Al_2O_3 , MgO , ZrO , TiO_2 , B_2O_3 , CaO , ZnO , BaO , and ThO_2 and by mixtures of the preceding such as $\text{SiO}_2\text{-MgO}$, $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-TiO}_2$, $\text{SiO}_2\text{-V}_2\text{O}_5$, $\text{SiO}_2\text{-Cr}_2\text{O}_3$, and $\text{SiO}_2\text{-TiO}_2\text{-MgO}$. Preferred among the preceding are microparticulate carriers whose main component is at least 1 component selected from the group consisting of SiO_2 and Al_2O_3 .

(0192)

The subject inorganic compound may also contain small amounts of a carbonate, sulfate, nitrate, or oxide component such as Na_2CO_3 , K_2CO_3 , CaCO_3 , MgCO_3 , Na_2SO_4 , $\text{Al}_2(\text{SO}_4)_3$, BaSO_4 , KNO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, Na_2O , K_2O , or Li_2O .

(0193)

While the properties of the microparticulate carrier (D) will vary as a function of its constituents and method of production, carriers preferred for use in the present invention desirably have a specific surface area of 50 to 1,000 m^2/g and preferably 100 to 700 m^2/g and desirably have a pore volume of 0.3 to 2.5 cm^3/g . As necessary, the subject carrier can be used after calcining at 100 to 1,000°C and preferably 150 to 700°C.

(0194)

Granular and microparticulate solid organic compounds with a particle size of 10 to 300 μm can also be used for the microparticulate carrier (D) employed by the present invention. These organic compounds can be exemplified by polymers and copolymers synthesized mainly from C_2 to C_{14} α -olefin, e.g., ethylene, propylene, 1-butene, and 4-methylpent-1-ene, and by polymers and copolymers synthesized mainly from vinylcyclohexane or styrene.

(0195)

In sum, then, the olefin polymerization catalyst according to the present invention comprises the above-described (A) Group 4 transition metal compound; (B) transition metal amide compound; (C) at least 1 compound selected from (C-1) organometal compounds, (C-2) organoaluminumoxy compounds, and (C-3) ionized ionic compounds; and optionally a microparticulate carrier (D).

(0196)

There are no restrictions on the method for using each component or on their order of addition in the execution of polymerization, but the following procedures can be provided as examples:

- (1) addition to the polymerization reactor in any sequence of components (A), (B), and (C);
- (2) addition to the polymerization reactor in any sequence of components (B) and (C) and a catalyst component comprising component (A) carried on support (D);
- (3) addition to the polymerization reactor in any sequence of components (A) and (C) and a catalyst component comprising component (B) carried on support (D);
- (4) addition to the polymerization reactor in any sequence of components (A) and (B) and a catalyst component comprising component (C) carried on support (D);
- (5) addition to the polymerization reactor in any sequence of component (C) and a catalyst component comprising components (A) and (B) carried on support (D);
- (6) addition to the polymerization reactor in any sequence of component (C), a catalyst component comprising component (A) carried on support (D), and a catalyst component comprising component (B) carried on support (D);

- (7) addition to the polymerization reactor in any sequence of component (B) and a catalyst component comprising components (A) and (C) carried on support (D);
- (8) addition to the polymerization reactor in any sequence of component (A) and a catalyst component comprising components (B) and (C) carried on support (D); and
- (9) addition to the polymerization reactor of a catalyst component comprising components (A), (B), and (C) carried on support (D).

(0197)

It is also possible in each of the above-listed methods (1)-(8) to carry out preliminary contact between or among two or more of the individual catalyst components. In each of methods (4), (7), (8), and (9) which use a supported component (C), unsupported component (C) — which may be the same as or different from the supported component (C) — may be added on an optional basis in any sequence.

(0198)

The aforementioned solid catalyst component comprising components (A) and (C) supported on component (D), solid catalyst component comprising components (B) and (C) supported on component (D), and solid catalyst component comprising components (A), (B), and (C) supported on component (D) can be prepolymerized with olefin. Catalyst component(s) can also be supported on a prepolymerized solid catalyst component.

(0199)

The olefin polymerization method according to the present invention produces olefin polymer by the polymerization or copolymerization of olefin in the presence of the olefin polymerization catalyst described hereinabove.

(0200)

Polymerization can be executed according to the present invention by a gas-phase polymerization method or by a liquid-phase polymerization method such as solution polymerization or suspension polymerization. The inert hydrocarbon medium used in liquid-phase polymerization methods can be specifically exemplified by aliphatic hydrocarbons such as propane, butane, pentane, hexane, heptane, octane, decane, dodecane, and kerosene; alicyclic hydrocarbons such as cyclopentane, cyclohexane, and methylcyclopentane; aromatic hydrocarbons such as benzene, toluene, and xylene; halogenated hydrocarbons such as

ethylene chloride, chlorobenzene, and dichloromethane; and mixtures of the preceding. The olefin itself can also be used as the solvent. Preferred among the aforementioned inert hydrocarbon media are aliphatic hydrocarbons and alicyclic hydrocarbons. Also preferred for use as the solvent are the α -olefin, alicyclic vinyl compound, and cyclic olefin actually used for polymerization.

(0201)

Olefin polymerization using the above-described olefin polymerization catalyst will in general use from 10^{-8} to 10^{-3} mol and preferably will use from 10^{-7} to 10^{-4} mol component (A) per 1 liter of reaction volume and will in general use from 10^{-8} to 10^{-2} mol and preferably will use from 10^{-7} to 10^{-3} mol component (B) per 1 liter of reaction volume. In addition, component (B) will be used in an amount that provides a molar ratio [(B)/(A)] between component (B) and component (A) in general from 0.02 to 100 and preferably from 0.05 to 50.

(0202)

Component (C-1) is used in an amount that provides a molar ratio [(C-1)/M] between component (C-1) and the total amount of transition metal atoms (M) in components (A) and (B) in general from 0.01 to 5,000 and preferably from 0.05 to 2,000.

(0203)

Component (C-2) is used in an amount that provides a molar ratio [(C-2)/M] between the aluminum atoms in component (C-2) and the total amount of transition metal atoms (M) in components (A) and (B) in general from 10 to 5,000 and preferably from 20 to 2,000.

(0204)

Component (C-3) is used in an amount that provides a molar ratio [(C-3)/M] between component (C-3) and the total amount of transition metal atoms (M) in components (A) and (B) in general from 1 to 10 and preferably from 1 to 5.

(0205)

The olefin polymerization temperature using the above-described olefin polymerization catalyst can generally be -50 to 200°C and preferably is 0 to 170°C . The polymerization pressure will generally be from atmospheric pressure to 100 kg/cm^2 and is preferably from atmospheric pressure to 50 kg/cm^2 . The polymerization reaction can be run by batch, semicontinuous, or continuous methods. The polymerization can also be divided into 2 or more stages with different reaction conditions.

(0206)

The molecular weight of the olefin polymer product can be controlled by the addition of hydrogen to the polymerization system or by varying the polymerization temperature. Olefin that can be polymerized using the olefin polymerization catalyst as described above can be exemplified by C₂ to C₂₀ α -olefin such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 3-methyl-1-butene, 3-methyl-1-pentene, 3-ethyl-1-pentene, 4-methyl-1-pentene, 4-methyl-1-hexene, 4,4-dimethyl-1-hexene, 4,4-dimethyl-1-pentene, 4-ethyl-1-hexene, 3-ethyl-1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and 1-eicosene; aromatic vinyl compounds such as styrene, the dimethylstyrenes, allylbenzene, the allyltoluenes, the vinylnaphthalenes, and the allylnaphthalenes; alicyclic vinyl compounds such as vinylcyclohexane, vinylcyclopentane, vinylcycloheptane, and allylnorbornane; cyclic olefins such as cyclopentene, cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene, and 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene; C₄ to C₂₀ chain polyenes such as 1,4-pentadiene, 1,5-hexadiene, 1,4-hexadiene, and 1,5,9-decatriene; and cyclic polyenes such as 5-ethylidenenorbornene and dicyclopentadiene.

(0207)

These olefins can be used singly or in combinations of two or more.

(0208)

Advantageous Effects of the Invention

The olefin polymerization catalyst according to the present invention exhibits a high polymerization activity and can produce olefin (co)polymer that has a broad molecular weight distribution and that, in the event of the copolymerization of two or more olefins, has a narrow composition distribution.

(0209)

The inventive olefin polymerization method can produce olefin polymer that has a broad molecular weight distribution and that, in the event of the copolymerization of two or more olefins, has a narrow composition distribution and achieves these results while exhibiting a high polymerization activity. The olefin (co)polymer produced by the inventive method exhibits an excellent moldability due to its broad molecular weight distribution.

(0210)

Examples

This invention is more specifically described hereinbelow through illustrative examples, but is not limited to these examples.

(0211)

The limiting viscosity ($[\eta]$) was measured in the illustrative examples in decalin at 135°C. The molecular weight distribution (Mw/Mn) was measured by gel permeation chromatography (GPC) at 140°C using o-dichlorobenzene as solvent.

(0212)

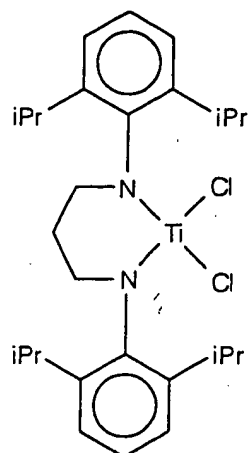
Example 1

5 mL toluene was introduced into a 20-mL glass container that had been thoroughly purged with nitrogen followed by the addition thereof of 0.1 mmol (as aluminum atoms) methylaluminumoxane, 0.1 micromol bis(1,3-dimethylcyclopentadienyl)zirconium dichloride, and 0.1 micromol titanium compound (B-1) with formula (a) given below. Stirring for 5 minutes gave a pre-contact catalyst (P-1).

(0213)

Separately from the above, 350 mL cyclohexane and then 150 mL 1-octene were introduced into a 1-liter stainless steel autoclave that had been thoroughly purged with nitrogen. 0.5 mmol triisobutylaluminum was then added and the temperature of the system was raised to 60°C. Polymerization was thereafter begun by injecting the entire quantity of the aforementioned pre-contact catalyst (P-1) using pressurized ethylene. Polymerization was carried out for 15 minutes at 70°C and a total pressure of 8 kg/cm²-G while continuously introducing ethylene. Polymerization was then stopped by the pressure injection of a small amount of methanol. The polymerization reaction solution was added to a large excess of methanol-hydrochloric acid solution to obtain a polymer, which was dried for 12 hours under reduced pressure at 130°C. This resulted in the recovery of 7.6 g of a polymer that gave the following values: $[\eta]$ = 3.97 dL/g and Mw/Mn = 5.2.

(0214)



(a)

(0215)

Comparative Example 1

Polymerization was carried out as in Example 1, but in this case without the use of the bis(1,3-dimethylcyclopentadienyl)zirconium dichloride. This resulted in the recovery of 3.6 g of a polymer that gave the following values: $[\eta] = 0.95$ dL/g and $M_w/M_n = 2.0$.

(0216)

Comparative Example 2

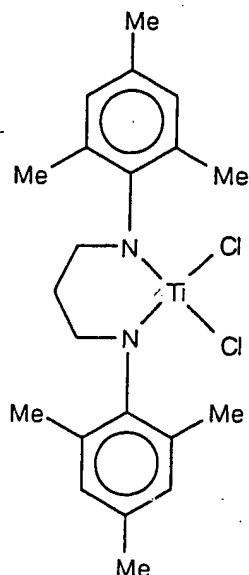
Polymerization was carried out as in Example 1, but in this case without using the titanium compound (B-1) and with the introduction of 50 mL hydrogen. This resulted in the recovery of 4.2 g of a polymer that gave the following values: $[\eta] = 2.93$ dL/g and $M_w/M_n = 2.9$.

(0217)

Example 2

Polymerization was carried out as in Example 1, but in this case using 0.1 micromol titanium compound (B-2) with formula (b) given below in place of the titanium compound (B-1). This resulted in the recovery of 7.5 g of a polymer that gave the following values: $[\eta] = 3.90$ dL/g and $M_w/M_n = 5.3$.

(0218)



(b)

(0219)

Comparative Example 3

Polymerization was carried out as in Example 1, but in this case omitting the bis(1,3-dimethylcyclopentadienyl)zirconium dichloride and using 0.1 micromol of the titanium compound (B-2) with the aforementioned formula (b) in place of the titanium compound (B-1). This resulted in the recovery of 3.4 g of a polymer that gave the following values: $[\eta] = 0.84$ dL/g and $M_w/M_n = 2.0$.

(0220)

Example 3

5 mL toluene was introduced into a 20-mL glass container that had been thoroughly purged with nitrogen followed by the addition thereto of 0.5 mmol (as aluminum atoms) methylaluminoxane, 0.4 micromol bis(1,3-dimethylcyclopentadienyl)hafnium dichloride, and 2 micromol bis[bis(trimethylsilyl)amido]zirconium dichloride $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{ZrCl}_2$. Stirring for 5 minutes gave a pre-contact catalyst (P-3).

(0221)

Separately from the above, 350 mL cyclohexane and then 150 mL 1-octene were introduced into a 1-liter stainless steel autoclave that had been thoroughly purged with nitrogen. 0.5 mmol

triisobutylaluminum was then added and the temperature of the system was raised to 60°C. Polymerization was thereafter begun by injecting the entire quantity of the aforementioned pre-contact catalyst (P-3) using pressurized ethylene. Polymerization was carried out for 15 minutes at 70°C and a total pressure of 8 kg/cm²-G while continuously introducing ethylene. Polymerization was then stopped by the pressure injection of a small amount of methanol. The polymerization reaction solution was added to a large excess of methanol-hydrochloric acid solution to obtain a polymer, which was dried for 12 hours under reduced pressure at 130°C. This resulted in the recovery of 6.7 g of a polymer that gave the following values: $[\eta] = 4.71$ dL/g and $M_w/M_n = 4.9$.

(0222)

Comparative Example 4

Polymerization was carried out as in Example 3, but in this case without the use of the bis(1,3-dimethylcyclopentadienyl)hafnium dichloride. This resulted in the recovery of 3.6 g of a polymer that gave the following values: $[\eta] = 2.37$ dL/g and $M_w/M_n = 1.9$.

(0223)

Comparative Example 5

Polymerization was carried out as in Example 3, but in this case without using the bis[bis(trimethylsilyl)amido]zirconium dichloride and with the introduction of 80 mL hydrogen. This resulted in the recovery of 3.3 g of a polymer that gave the following values: $[\eta] = 2.88$ dL/g and $M_w/M_n = 3.0$.

(0224)

Example 4

5 mL toluene was introduced into a 20-mL glass container that had been thoroughly purged with nitrogen followed by the addition thereto of 0.5 micromol triisobutylaluminum, 0.4 micromol bis(1,3-dimethylcyclopentadienyl)hafnium dichloride, 0.1 micromol of the titanium compound (B-2) with the aforementioned formula (b), and 1 micromol triphenylcarbenium tetrakis(pentafluorophenyl)borate in the given sequence. Stirring for 5 minutes gave a pre-contact catalyst (P-4).

(0225)

Separately from the above, 350 mL cyclohexane and then 150 mL 1-octene were introduced into a 1-liter stainless steel autoclave that had been thoroughly purged with nitrogen. 0.5 mmol triisobutylaluminum was then added and the temperature of the system was raised to 60°C. Polymerization was thereafter begun by injecting the entire quantity of the aforementioned pre-contact catalyst (P-4) using pressurized ethylene. Polymerization was carried out for 15 minutes at 70°C and a total pressure of 8 kg/cm²-G while continuously introducing ethylene. Polymerization was then stopped by the pressure injection of a small amount of methanol. The polymerization reaction solution was added to a large excess of methanol-hydrochloric acid solution to obtain a polymer, which was dried for 12 hours under reduced pressure at 130°C. This resulted in the recovery of 7.3 g of a polymer that gave the following values: $[\eta] = 4.62$ dL/g and $M_w/M_n = 5.4$.

(0226)

Comparative Example 6

Polymerization was carried out as in Example 4, but in this case without the use of the bis(1,3-dimethylcyclopentadienyl)hafnium dichloride. This resulted in the recovery of 3.7 g of a polymer that gave the following values: $[\eta] = 1.29$ dL/g and $M_w/M_n = 2.1$.

(0227)

Comparative Example 7

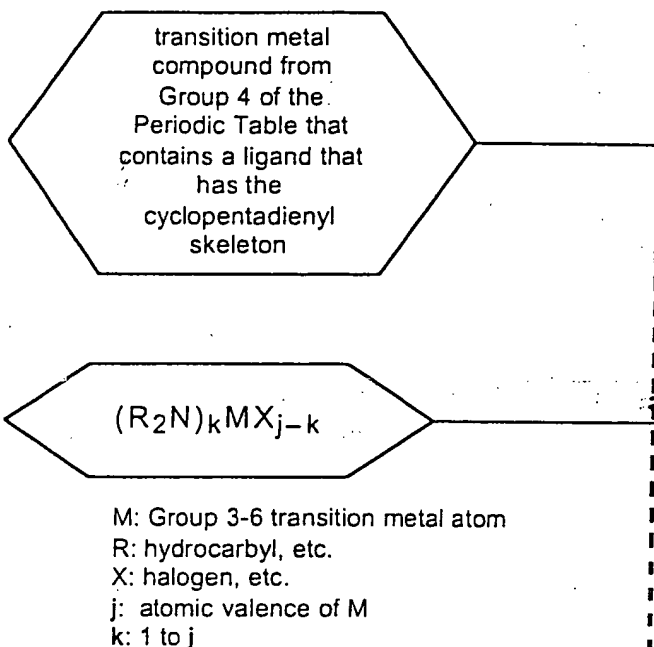
Polymerization was carried out as in Example 4, but in this case without using the titanium compound (B-2) and with the introduction of 80 mL hydrogen. This resulted in the recovery of 3.6 g of a polymer that gave the following values: $[\eta] = 3.04$ dL/g and $M_w/M_n = 3.1$.

Brief Description of the Drawings

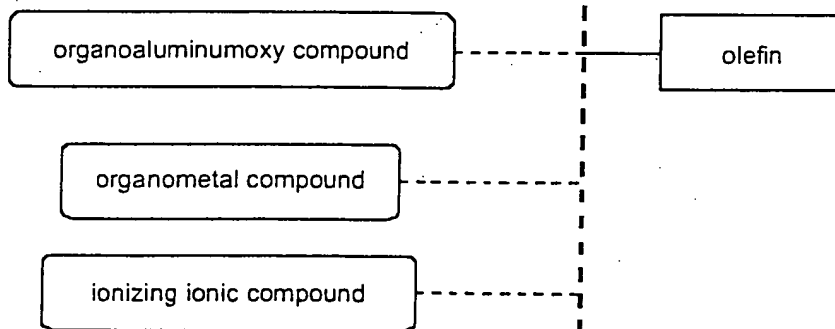
Figure 1 is a descriptive drawing that illustrates the process for preparing the olefin polymerization catalyst of the present invention.

Figure 1.

(A) Transition metal component



(B) Organometal component



(C) Third component

(microparticulate carrier)